

N 7 2 2 2 6 8 2

STRUCTURAL EXPANSIONS FOR THE GROUND STATE ENERGY  
OF A SIMPLE METAL

J. Hammerberg and N. W. Ashcroft

Laboratory of Atomic and Solid State Physics  
Cornell University  
Ithaca, New York 14850

**CASE FILE -  
COPY**

January 1973

Report #1943

Issued by the Materials Science Center

Structural Expansions for the Ground State Energy  
of a Simple Metal\*

J. Hammerberg and N. W. Ashcroft

Laboratory of Atomic and Solid State Physics  
Cornell University  
Ithaca, New York 14850

Abstract

A structural expansion for the static ground state energy of a simple metal is derived. Two methods are presented, one an approach based on single particle band structure which treats the electron gas as a non-linear dielectric, the other a more general many particle analysis using finite temperature perturbation theory. The two methods are compared, and it is shown in detail how band-structure effects, Fermi surface distortions, and chemical potential shifts affect the total energy. These are of especial interest in corrections to the total energy beyond third order in the electron ion interaction and hence to systems where differences in energies for various crystal structures are exceptionally small. Preliminary calculations using these methods for the zero temperature thermodynamic functions of atomic hydrogen are reported.

## I. INTRODUCTION

Recent work in the theory of metallic phase stability has met with moderate success in accounting for the most stable crystalline structure, binding energy, and compressibility of a simple metal.<sup>1,2</sup> The theory depends upon a perturbation expansion of the ground state energy ( $T = 0^\circ\text{K}$ ), usually to second order in the Fourier components of the pseudopotential evaluated at reciprocal lattice vectors. In certain cases, however, the energy difference between structures is so small that it is essential to consider higher order terms in a structural expansion for the energy. A case in point is atomic metallic hydrogen for which a second order calculation of the ground state energy per proton using a RPA dielectric function gives (static lattice) energies of -1.01532, -1.01597, and -1.01537 Ry respectively for the SC, FCC and BCC structures at a density ( $r_s = 1.6$ ) near the zero pressure metastable equilibrium.

The procedures for constructing the perturbation expansion have been known since 1958 when Hubbard<sup>3</sup> developed a diagrammatic technique based upon solutions of a one-electron Hartree-like equation, a method which ultimately enabled him to express the energy in terms of the solutions to an integral equation. Later, self-consistent methods were proposed by Cohen<sup>4</sup> who treated the ground state properties of a solid along the lines of the dielectric formulation of Nozières and Pines<sup>5</sup> for the

electron gas. More recently Brovman et al.<sup>6</sup> have used a modification of Hubbard's technique to calculate both binding energies and phonon spectra for simple metals. Lloyd and Sholl<sup>7</sup> have also presented explicit expressions for third order corrections to the total energy using an analysis similar to that of Hohenberg and Kohn<sup>8</sup>, and Harrison<sup>9</sup> has discussed the interpretation of these contributions in terms of three body interactions. What we present here is an explicit structural expansion which is convenient for calculation of ground state energy as a function of density and which is simply related to the eigenvalues of the one-electron band Hamiltonian. We shall discuss its relation to a more complete solution given in terms of the  $T = 0^\circ\text{K}$  limit of finite temperature perturbation theory. Finally we shall discuss certain differences between the present work and the previous theories mentioned above and apply these techniques to a calculation of the ground state properties of atomic hydrogen. A comprehensive Bravais lattice survey of the binding energy to third order in electron ion interaction for this solid has been carried out by Brovman et al.<sup>10</sup>. The purpose of our calculations is rather to study the magnitudes of higher order corrections, in support of which we shall present numerical values for SC, FCC, and BCC lattices.

## II. FORMULATION OF THE PROBLEM

We consider in this section the problem of computing the total energy of a system of  $N$  interacting electrons in a static periodic one body potential. Later<sup>11</sup> we shall relax this restriction and consider the modifications arising from dynamic effects. To begin with we shall restrict our considerations to  $T = 0^\circ\text{K}$  and subsequently extend the analysis to non-zero temperatures.

The Hamiltonian for our system thus restricted may be written as

$$H = H_{ee} + H_{ei} + H_{ii} \quad (1)$$

where  $H_{ee}$  describes the kinetic and interaction energy of a system of coupled electrons, i.e.

$$H_{ee} = \frac{1}{2m} \sum_i p_i^2 + \frac{1}{2} \sum_{i,j}' \frac{e^2}{|\tilde{r}_i - \tilde{r}_j|} \quad , \quad (2)$$

$H_{ii}$  describes the interaction energy of the rigid lattice of ions of valence  $Z$ , i.e.

$$H_{ii} = \frac{1}{2} \sum_{\alpha,\beta} W(\tilde{R}_\alpha, \tilde{R}_\beta) \quad , \quad (3)$$

and  $H_{ei}$  describes the interaction of electrons with the lattice, i.e.

$$H_{ei} = \sum_i V(\tilde{r}_i) \quad . \quad (4)$$

In (3)  $W(\tilde{R}_1, \tilde{R}_2)$  is the bare ion-ion interaction, and in (4)

$V(\underline{r})$  is the periodic one body potential. We may express  $H_{ee}$  in terms of second quantized operators, i.e.

$$\frac{1}{2m} \sum_i p_i^2 \rightarrow \frac{\hbar^2}{2m} \sum_{\underline{k}} k^2 c_{\underline{k}}^+ c_{\underline{k}} \quad (5)$$

$$\frac{1}{2} \sum_{i,j}' \frac{e^2}{|\underline{r}_i - \underline{r}_j|} \rightarrow \frac{1}{2} \sum_{\underline{k}, \underline{k}', \underline{q}} w(\underline{q}) c_{\underline{k}+\underline{q}}^+ c_{\underline{k}'-\underline{q}}^+ c_{\underline{k}'} c_{\underline{k}} \quad (6)$$

where

$$\Omega w(\underline{q}) = \int_{\Omega} e^{-i\underline{q} \cdot \underline{r}} \frac{e^2}{r} d^3 r = \frac{4\pi e^2}{q^2}, \quad (7)$$

is the Fourier transform of the bare Coulomb interaction ( $\Omega$  being the volume of the system<sup>12</sup>). There is the usual problem of handling the  $q = 0$  term. To resolve it we carry out the following series of manipulations (the thermodynamic limit being taken as the ultimate step). First, we subtract from  $H_{ee}$  the term

$$\Omega \frac{1}{2} e^2 \left( \frac{N}{\Omega} \right)^2 \int_{\Omega} \frac{1}{r} d^3 r, \quad (8)$$

that is, the interaction term in  $H_{ee}$  is replaced by

$$\frac{1}{2} \sum_{i,j}' \left[ \frac{e^2}{|\underline{r}_i - \underline{r}_j|} - \frac{e^2}{\Omega} \int_{\Omega} \frac{1}{r} d^3 r \right], \quad (9)$$

and  $H_{ee}$  accordingly becomes

$$H_{ee} \rightarrow \frac{1}{2m} \sum_{\underline{k}} \hbar^2 k^2 c_{\underline{k}}^+ c_{\underline{k}} + \frac{1}{2} \sum_{\substack{\underline{k}, \underline{k}' \\ \underline{q} \neq \underline{0}}} w(\underline{q}) c_{\underline{k}+\underline{q}}^+ c_{\underline{k}'-\underline{q}}^+ c_{\underline{k}'} c_{\underline{k}} \quad (10)$$

which is the familiar electron gas Hamiltonian, denoted in what

follows by  $H_{eg}$ . We now add (8) to  $H_{ii}$ . Thus

$$H_{ii} \rightarrow \sum_{\alpha\beta} W(R_\alpha, R_\beta) + \frac{1}{2} \int \frac{\rho_o^2}{|r_1 - r_2|} d^3r_1 d^3r_2, \quad (11)$$

where  $\rho_o = \frac{Ne}{\Omega}$ . The term which has been added is the self-energy of a uniform background of negative (or positive) charge. To (11) we add the interaction energy of the ions with this negative background so that  $H_{ii}$  becomes

$$H_{ii} \rightarrow \frac{1}{2} \sum_{\alpha\beta} W(\tilde{r}_\alpha, \tilde{r}_\beta) + \frac{1}{2} \int \frac{\rho_o^2}{r_{12}} d^3r_1 d^3r_2 - \sum_{\alpha} \int \rho_o W(\tilde{r}, \tilde{r}_\alpha) d^3r, \quad (12)$$

which, if we neglect Born-Mayer terms, is just the Madelung energy for the assembly of ions. Finally, we subtract the same interaction energy from the last term in  $H$ ,  $H_{ei}$ , obtaining

$$H_{ei} \rightarrow \sum_i V(\tilde{r}_i) + \sum_{\alpha} \int \rho_o W(\tilde{r}, \tilde{r}_\alpha) d^3r. \quad (13)$$

The original Hamiltonian has now been separated into three well defined parts. Taking its average over the ground state we have as the expression for the total energy per electron,

$$\frac{E}{N} = \frac{1}{N} \{ \langle H_{eg} \rangle + \langle H_{ei} \rangle \} + E_M \quad (14)$$

where  $E_M$  is the Madelung energy, i.e. the energy per electron of a lattice of positive ions in a uniform background of negative charge. Notice that the first term in (14) is not the energy per electron of the interacting electron gas since the ground

state wavefunction is that appropriate to an electron gas in which a periodic array of ions is immersed.

Let us consider the second term in more detail. For even a simple metal the interaction potential  $V(\underline{r})$  is not known in general from first principles. From the point of view of band theory, however, it may be well represented by a weak pseudopotential, at least for the valence states. (We set aside in this discussion questions of core level shifts and their effect on the total energy.) If we make this pseudopotential approximation and furthermore consider a local approximation in which the periodic potential is a simple superposition of bare pseudopotentials at each lattice site, then (13) becomes

$$H_{ei} = \sum_{i\alpha} v(\underline{r}_i - \underline{R}_\alpha) + \sum_{\alpha} \int_{\Omega} \frac{Ze\rho_o}{|\underline{r} - \underline{R}_\alpha|} d^3r, \quad (15)$$

or in terms of the Fourier transform of  $v$ ,

$$H_{ei} = \sum_{\underline{k}, i} \rho_{\underline{k}}^{(i)} v(\underline{k}) e^{i\underline{k} \cdot \underline{r}_i} + \sum_{\alpha} \int_{\Omega} \frac{Ze\rho_o}{r} d^3r, \quad (16)$$

where

$$\Omega v(\underline{k}) = \int_{\Omega} v(\underline{r}) e^{-i\underline{k} \cdot \underline{r}} d^3r, \quad (17)$$

and

$$\rho_{\underline{k}}^{(i)} = \sum_{\alpha} e^{-i\underline{k} \cdot \underline{R}_\alpha}. \quad (18)$$



In particular, the  $\tilde{k} = 0$  term is given by

$$\lim_{\tilde{k} \rightarrow 0} \left[ N_i N v(\tilde{k}) + N_i Z e \rho_0 \int_{\Omega} \frac{d^3 r}{r} \right] , \quad (19)$$

where  $N_i$  is the number of ions,  $N = Z N_i$ . As an example, for a potential which is Coulombic beyond a certain "core" radius  $r_c$ <sup>13</sup> and vanishes otherwise we have

$$\lim_{\tilde{k} \rightarrow 0} v(\tilde{k}) = -Z e^2 \int_{r_c}^{\infty} \frac{d^3 r}{r} + \int_0^{r_c} v(\tilde{r}) d^3 r . \quad (20)$$

Hence the long range parts in (19) cancel and we are left with

$$H_{ei} = \sum_{\substack{\tilde{k} \neq 0 \\ i}} \rho_{\tilde{k}}^{(i)} v(\tilde{k}) e^{i \tilde{k} \cdot \tilde{r}_i} + N \frac{N_i}{\Omega} \int_0^{r_c} v(\tilde{r}) d^3 r + N Z e \rho_0 \int_0^{r_c} \frac{d^3 r}{r} , \quad (21)$$

which we rewrite as

$$H_{ei} = \sum'_{i, \tilde{k}} \rho_{\tilde{k}}^{(i)} v(\tilde{k}) e^{i \tilde{k} \cdot \tilde{r}_i} + N E_c , \quad (22)$$

where the "core" contribution<sup>14</sup>  $E_c$  is independent of structure, and the prime means that  $\tilde{k} = 0$  is excluded from the summation.

Thus the ground state energy ( $T = 0^\circ K$ ) can be written in

the form

$$\frac{E}{N} = \frac{1}{N} \langle H_{eg} \rangle + \frac{1}{N} \langle \sum_{\tilde{k}}' \rho_{\tilde{k}}^{(i)} v(\tilde{k}) \rho_{-\tilde{k}} \rangle + E_c + E_M , \quad (23)$$

where  $\rho_{-\tilde{k}} = \sum_i e^{i \tilde{k} \cdot \tilde{r}_i}$ . For a lattice of bare protons, we note that (23) is exact with  $E_c = 0$  and  $v(\tilde{k}) = w(\tilde{k})$ . However, for the general case it is approximate since it is not clear that

a single-particle equation describing the band structure with a local  $v(\underline{r})$  can be derived from  $H$  as given in (23) with the same  $v(\underline{r})$ . Moreover, it is not strictly correct to write the lattice potential as a simple superposition. With these reservations, we may address ourselves to the task of computing the average

$$\frac{1}{N} \langle H_{eg} + \sum_{\underline{k}} \rho_{\underline{k}}^{(i)} v(\underline{k}) \rho_{-\underline{k}} \rangle \quad . \quad (24)$$

If we treat  $H_1 \equiv \sum_{\underline{k}} \rho_{\underline{k}}^{(i)} v(\underline{k}) \rho_{-\underline{k}}$  as a perturbation, then the unperturbed problem is the interacting electron gas. Indeed, the problem is that of a dense distribution of identical impurities in the electron gas except that for a crystal, the impurities are arrayed in a definite order. Alternatively, one may simultaneously treat both electron-electron and electron-ion interactions as perturbations and carry out the usual double perturbation expansion. In the following sections we present two methods for computing the energy shift due to  $H_1$ , one closely related to a single particle picture, the other a more general many particle method.

### III. BAND APPROACH

In this section we consider the calculation of the ground state energy from a single particle point of view. The physical picture is the following. We have a system of electrons whose interactions with the static lattice are described by a pseudo-potential. The electron gas may be viewed as a non-linear dielectric and the pseudo-ions as the source of external potentials which induce charge density responses in it. The energy associated with this induction process is given by the well known expression<sup>15</sup>

$$\delta W = \int \delta V(\underline{r}) \rho(\underline{r}) d^3 r \quad (25)$$

This is the work which an external contrivance must do in changing the potentials from some value  $V$  to  $V + \delta V$ . In terms of Fourier transformed quantities this becomes

$$\delta W = \Omega \sum_{\underline{k}} \delta V(-\underline{k}) \rho(\underline{k}) . \quad (26)$$

The contribution of the electron-ion interaction to the total energy is then given by

$$W = \int_0^V \delta W \quad (27)$$

In general, we may write the charge density  $\rho(\underline{k})$  as

$$\begin{aligned} \rho(\underline{k}) = & \chi_1(\underline{k}) V(\underline{k}) + \sum_{\underline{q}} \chi_2(\underline{k}, \underline{q}) V(\underline{k} + \underline{q}) V(-\underline{q}) \\ & + \sum_{\underline{q}_1, \underline{q}_2} \chi_3(\underline{k}, \underline{q}_1, \underline{q}_2) V(\underline{k} + \underline{q}_1 + \underline{q}_2) V(-\underline{q}_1) V(-\underline{q}_2) + \dots, \end{aligned} \quad (28)$$

the first term of which is the usual linear response expression. In appendix A we show that this leads to an expression for the change in energy given by

$$\begin{aligned} \frac{N}{\Omega} E_b \equiv W = & \frac{1}{2} \sum_{\underline{k}} \chi_1(\underline{k}) V(-\underline{k}) V(\underline{k}) + \frac{1}{3} \sum_{\underline{k}, \underline{q}} \chi_2(\underline{k}, \underline{q}) V(\underline{k}+\underline{q}) V(-\underline{q}) V(-\underline{k}) \\ & + \frac{1}{4} \sum_{\underline{k}, \underline{q}_1, \underline{q}_2} \chi_3(\underline{k}, \underline{q}_1, \underline{q}_2) V(\underline{k}+\underline{q}_1+\underline{q}_2) V(-\underline{q}_1) V(-\underline{q}_2) V(-\underline{k}) + \dots \end{aligned} \quad (29)$$

which we shall refer to as the band structure energy<sup>16</sup> and which is determined from the induced charge density through (28). Note that  $V(0)$  is to be excluded from the summation (a requirement of charge neutrality as discussed in section II). Equation (29) thus presents us with a well defined method for calculating  $E_b$  in terms of the charge density.

From the point of view of single particle band theory we calculate the charge density from the Bloch wave function of an electron in a periodic potential  $\tilde{V}$ . In terms of plane waves

$$\langle \underline{r} | \underline{k}-\underline{K} \rangle = \Omega^{-\frac{1}{2}} e^{i(\underline{k}-\underline{K}) \cdot \underline{r}} \quad (30)$$

the wave function is written as (we assume a Bravais lattice)

$$|\psi_{\underline{k}} \rangle = \sum_{\underline{K}} c_{\underline{k}-\underline{K}} |\underline{k}-\underline{K} \rangle \equiv \sum_{\underline{i}} c_{\underline{i}} |\underline{i} \rangle, \quad (31)$$

where the coefficients  $c_{\underline{i}}$  satisfy the equations

$$\begin{aligned}
 (\mathcal{E}_0 - E + \tilde{V}_{00})c_0 + \tilde{V}_{01}c_1 + \sum_{i \neq 0,1} \tilde{V}_{0i}c_i &= 0 \\
 \tilde{V}_{10}c_0 + (\mathcal{E}_1 - E + \tilde{V}_{11})c_1 + \sum_{i \neq 0,1} \tilde{V}_{1i}c_i &= 0 \\
 \dots & \dots \\
 \tilde{V}_{i0}c_0 + \tilde{V}_{i1}c_1 + (\mathcal{E}_i - E + \tilde{V}_{ii})c_i + \sum_{j \neq 0,1,i} \tilde{V}_{ij}c_j &= 0 \\
 \dots & \dots
 \end{aligned} \tag{32}$$

with  $\mathcal{E}_i = \frac{\hbar^2}{2m} (\tilde{k} - \tilde{K}_i)^2$  and  $\tilde{V}_{ij} = \langle \tilde{k} - \tilde{K}_i | \tilde{V} | \tilde{k} - \tilde{K}_j \rangle$ . An iterative solution of equations (32) yields a Brillouin-Wigner expansion for the  $c_i$  namely:

$$\begin{aligned}
 c_i &= c_0 \left\{ \frac{\tilde{V}_{i0}}{E - \mathcal{E}_i} + \sum_j' \frac{\tilde{V}_{ij} \tilde{V}_{j0}}{(E - \mathcal{E}_i)(E - \mathcal{E}_j)} + \sum_{jk}' \frac{\tilde{V}_{ij} \tilde{V}_{jk} \tilde{V}_{k0}}{(E - \mathcal{E}_i)(E - \mathcal{E}_j)(E - \mathcal{E}_k)} + \dots \right\} \\
 &+ c_1 \left\{ \frac{\tilde{V}_{i1}}{E - \mathcal{E}_i} + \sum_j' \frac{\tilde{V}_{ij} \tilde{V}_{j1}}{(E - \mathcal{E}_i)(E - \mathcal{E}_j)} + \sum_{jk}' \frac{\tilde{V}_{ij} \tilde{V}_{jk} \tilde{V}_{k1}}{(E - \mathcal{E}_i)(E - \mathcal{E}_j)(E - \mathcal{E}_k)} + \dots \right\}, \tag{33}
 \end{aligned}$$

where the prime excludes 0,1. Equations (33) lead to a folded secular equation

$$\begin{aligned}
 (\mathcal{E} - E + U_{00})c_0 + U_{01}c_1 &= 0 \\
 U_{10}c_0 + (\mathcal{E}_1 - E + U_{11})c_1 &= 0
 \end{aligned} \tag{34}$$

with the  $U$ 's defined by

$$U_{\ell m} = \tilde{V}_{\ell m} + \sum_i' \frac{\tilde{V}_{\ell i} \tilde{V}_{im}}{E - \mathcal{E}_i} + \sum_{ij}' \frac{\tilde{V}_{\ell i} \tilde{V}_{ij} \tilde{V}_{jm}}{(E - \mathcal{E}_i)(E - \mathcal{E}_j)} + \dots \tag{35}$$

In (35) the prime excludes  $\ell, m$  from the summations. Note

that although  $U_{\ell m}^* = U_{m\ell}$ ,  $U_{\ell-m,0} \neq U_{\ell m}$ . The folding transformation

is valid for any  $l, m$  and accordingly,

$$\begin{aligned} (\mathcal{E}_l + U_{ll} - E)c_l + U_{lm}c_m &= 0 \\ U_{ml}c_l + (\mathcal{E}_m + U_{mm} - E)c_m &= 0 \end{aligned} \quad (36)$$

These equations define a two band (upper<sup>(+)</sup> and lower<sup>(-)</sup>) situation for which the solution for  $K_1 \Rightarrow 0$  is:

$$\begin{aligned} E_{(-)} &= \mathcal{E}_o + U_{oo}^{(-)} + |U_{om}^{(-)}| \left\{ \gamma_m^{(-)} - (1 + (\gamma_m^{(-)})^2)^{\frac{1}{2}} \right\} \\ \gamma_m^{(-)} &\equiv \frac{1}{2|U_{om}^{(-)}|} \left\{ \mathcal{E}_m - \mathcal{E}_o + U_{mm}^{(-)} - U_{oo}^{(-)} \right\} \end{aligned} \quad (37)$$

$$c_m^{(-)} = \frac{U_{mo}^{(-)} c_o^{(-)}}{(\mathcal{E}_m + U_{mm}^{(-)} - E_{(-)})} = - \frac{(\mathcal{E}_m + U_{oo}^{(-)} - E_{(-)})}{U_{om}^{(-)}} c_o^{(-)}$$

or

$$c_m^{(-)} = \frac{|U_{om}^{(-)}|}{U_{om}^{(-)}} \left\{ \gamma_m^{(-)} - (1 + (\gamma_m^{(-)})^2)^{\frac{1}{2}} \right\} c_o^{(-)} \quad (38)$$

A similar expression holds for the upper band with  $(-) \rightarrow (+)$  and  $\left\{ \gamma_m^{(-)} - (1 + (\gamma_m^{(-)})^2)^{\frac{1}{2}} \right\} \rightarrow \left\{ \gamma_m^{(+)} + (1 + (\gamma_m^{(+)} )^2)^{\frac{1}{2}} \right\}$ . We may use these results to calculate a charge density, i.e.

$$\rho(\underline{r}) = 2 \sum_{[\underline{k}]} \sum_{ij} c_i^* c_j < i | \underline{r} > < \underline{r} | j > , \quad (39)$$

where  $\sum_{[\underline{k}]}$  denotes a summation restricted to occupied levels.

The Fourier transform of (39) gives

$$\rho_l = \frac{2}{\Omega} \sum_{[\underline{k}]} \sum_i c_i^* c_{i-l} \quad (40)$$

which for a single occupied band reads

$$\rho_l = \frac{2}{\Omega} \sum_{[k]} \sum_i \frac{\{\gamma_i - (1+\gamma_i^2)^{\frac{1}{2}}\} \{\gamma_{i-l} - (1+\gamma_{i-l}^2)^{\frac{1}{2}}\}}{\left\{1 + \sum_{j \neq 0} \{\gamma_j - (1+\gamma_j^2)^{\frac{1}{2}}\}^2\right\}} \quad (41)$$

Alternatively, this may be rewritten using (37) as

$$\rho_l = \frac{2}{\Omega} \sum_{[k]} \frac{\left\{ \frac{2U_{ol}}{(E_k - \epsilon_l - U_{ll})} + \sum_{i \neq 0, l} \frac{U_{i-l, o} U_{i, o}^*}{(E_k - \epsilon_{i-l} - U_{i-l, i-l}) (E_k - \epsilon_i - U_{ii})} \right\}}{\left\{ 1 + \sum_{j \neq 0} \frac{|U_{jo}|^2}{(E_k - \epsilon_j - U_{jj})^2} \right\}} \quad (42)$$

These last two expressions are easily generalized if two bands are occupied. If more than two bands are occupied it is necessary to begin with the folded secular equation appropriate to that number. We note again that in (41) the  $k$  summation is only over occupied levels. Thus we are summing up to the true Fermi surface rather than within a Fermi sphere (the more common situation in perturbation theory).

The above expressions although formally exact within the one electron approximation are difficult to use in practice. If we knew the analytic dependence of the  $U$ 's on  $\tilde{V}$  we could perform the integration in (27) (for example, by associating with  $\tilde{V}$  a coupling constant over which we ultimately integrate) and finally carry out the sum on  $k$ . However, only in the extreme approximation of retaining a single  $\gamma$  is this analytically

tractable. We can, on the other hand, expand the expression for  $\rho_{\ell}$  in powers of  $\tilde{V}$ . If we then assume that  $\tilde{V}(\underline{k}) = V(\underline{k})/\epsilon(\underline{k})$  where  $\epsilon(\underline{k})$  is the static limit of the electron gas dielectric function, it is possible to calculate the energy shift from (29). The results of such an expansion are given in appendix B. In the following section we shall derive an expression for the energy shift from a more complete theory and see that the simple theory above must be only slightly modified.



#### IV. FINITE TEMPERATURE RESULTS

In this section we calculate the total energy of the system of electrons and ions using the techniques of finite temperature perturbation theory. If we choose as the unperturbed system one having a spherical Fermi surface (e.g. non-interacting or interacting electron gas), it is, in fact, necessary to use this method, a consequence of the fact that for interacting electrons in a periodic potential, the adiabatically generated state of the zero temperature method is not the true ground state, no matter how weak the lattice potential. The state generated adiabatically from a spherical ground state can never depart from a state with a spherical Fermi surface and cannot produce the crossing of levels<sup>17,18</sup> resulting from the imposition of a periodic potential. In the finite temperature theory, however, the mean occupation number of a given quantum state is no longer restricted to be either 0 or 1. Thus the Fermi surface of the unperturbed system is permitted to distort in such a way that the thermodynamic potential is minimized subject to the constraint of fixed overall density and in consequence the true Fermi surface is attained at each stage of the calculation.

The temperature formalism is most simply stated in terms of Green functions. We shall follow the exposition of Martin and Schwinger<sup>19</sup> and define the single particle Green function as

$$G_{\alpha\beta}(\underline{r}_1, t_1; \underline{r}_2, t_2) = (-i) \langle T \psi_{\alpha}(\underline{r}_1, t_1) \psi_{\beta}^{\dagger}(\underline{r}_2, t_2) \rangle \quad (43)$$

where the brackets denote the grand canonical ensemble average

$$\langle \mathcal{O} \rangle = \frac{\text{Tr } e^{-\beta(H-\mu N)} \mathcal{O}}{\text{Tr } e^{-\beta(H-\mu N)}} \quad (44)$$

$\psi, \psi^{\dagger}$  are Heisenberg field operators,  $\alpha, \beta$  are spin indices and  $T$  is the time ordering operator for real  $t$  (and the 'it' ordering operator for imaginary times.) We Fourier transform  $G$  and write the result itself as a Fourier series

$$G_{\alpha\beta}(\underline{p}_1, \underline{p}_2; t) \equiv \frac{1}{2} \int_{\Omega} d^3 r_1 d^3 r_2 e^{-i \underline{p}_1 \cdot \underline{r}_1} e^{i \underline{p}_2 \cdot \underline{r}_2} G_{\alpha\beta}(\underline{r}_1, \underline{r}_2; t) \quad (45)$$

$$G_{\alpha\beta}(\underline{p}_1, \underline{p}_2; t) = \frac{1}{(-i\beta)} \sum_{\nu} e^{-i\omega_{\nu} t} G_{\alpha\beta}(\underline{p}_1, \underline{p}_2; \omega_{\nu}) \quad (0 \leq it \leq \beta) \quad (46)$$

where  $\omega_{\nu} = \frac{\pi}{(-i\beta)} (2\nu + 1) + \mu$ ,  $\nu = 0, \pm 1, \dots$ , so that

$$G_{\alpha\beta}(\underline{p}_1, \underline{p}_2; \omega_{\nu}) = \int_0^{(-i\beta)} G_{\alpha\beta}(\underline{p}_1, \underline{p}_2; t) dt \quad (47)$$

These results are consequences of the boundary condition satisfied by  $G$  for imaginary times. The average value of a one-body operator is given in terms of the Green function by

$$\langle v \rangle = \frac{1}{\beta} \sum_{\underline{p}, \underline{k}, \nu} v(-\underline{p})_{\Omega} G_{\alpha\alpha}(\underline{k}, \underline{k}-\underline{p}; \omega_{\nu}) e^{\omega_{\nu} 0^+} \quad (48)$$

(where for the sake of brevity  $G_{\alpha\alpha} \equiv \sum_{\alpha} G_{\alpha\alpha}$ ).

In order to compute the ground state energy we use the statistical mechanical theorem<sup>20</sup> which states that for any parameter  $\lambda$  in the Hamiltonian,

$$\frac{\partial \Xi}{\partial \lambda} = \langle \frac{\partial H(\lambda)}{\partial \lambda} \rangle, \quad (49)$$

where  $\Xi$  is the thermodynamic potential, the differentiation is at fixed  $T$ ,  $V$ ,  $\mu$ , and the average is that defined in (44).

For the Hamiltonian we take that given in (24). If we associate a coupling constant  $\lambda$  with the bare interaction  $V$ , we then have upon integration,

$$\Xi(\mu) = \Xi_0(\mu) + \int_0^1 \frac{d\lambda}{\lambda} \langle \lambda V \rangle_\lambda. \quad (50)$$

To calculate the ground state energy we take the  $T = 0$  limit of  $\Xi(\mu) + \mu \bar{N}$ , i.e.

$$\bar{N}E' = \lim_{T \rightarrow 0} \left\{ \Xi_0(\mu) + \mu \bar{N} \right\} + \int_0^1 \frac{d\lambda}{\lambda} \langle \lambda V \rangle_\lambda, \quad (51)$$

which we write as

$$\begin{aligned} E' &= E_0 + E_b \\ E_0 &= \frac{1}{\bar{N}} \lim_{T \rightarrow 0} \left\{ \Xi_0(\mu) + \mu \bar{N} \right\} \\ E_b &= \frac{1}{\bar{N}} \lim_{T \rightarrow 0} \int_0^1 \frac{d\lambda}{\lambda} \langle \lambda V \rangle_\lambda. \end{aligned} \quad (52)$$

The ground state energy is then

$$E = E_0 + E_b + E_M + E_c \quad (53)$$

We note that  $E_0$  is not the ground state energy of the electron

gas at density  $\bar{N}/\Omega$  since the chemical potential  $\mu$  is that appropriate to the complete system, namely electrons and ions. But  $E_b$  has the same form as that derived in section III, for we may expand  $G(\underline{k}, \underline{q}, \omega_v)$  in a Laurent series.

$$\Omega G(\underline{k}, \underline{q}; \omega_v) = \sum_{n=0}^{\infty} \lambda^n G^{(n)}(\underline{k}, \underline{q}; \omega_v) \quad (54)$$

so that, using (48),

$$\langle \lambda V \rangle_{\lambda} = \frac{2}{\beta} \sum_{\underline{p}, \underline{k}, \nu} \sum_{n=0}^{\infty} V(-\underline{p}) \lambda^{n+1} G^{(n)}(\underline{k}, \underline{k}-\underline{p}; \omega_v) e^{\omega_v} 0^+ \quad (55)$$

and the expression for  $E_b$  now reads<sup>21</sup>

$$E_b = \lim_{T \rightarrow 0} \frac{1}{\bar{N}} \sum_{n=0}^{\infty} \frac{1}{n+2} \frac{2}{\beta} \sum_{\underline{p}, \underline{k}, \nu} V(-\underline{p}) G^{(n+1)}(\underline{k}, \underline{k}-\underline{p}; \omega_v) e^{\omega_v} 0^+, \quad (56)$$

which is of the same form as (29) and constitutes a more formal derivation of it.

In order to calculate  $E_b$  we need explicit expressions for the quantities  $G^{(n+1)}$ . Considering the lowest order term we note that  $G^{(1)}$  can be calculated in terms of known electron gas quantities. We have

$$G^{(1)}(\underline{k}, \underline{k}-\underline{p}; \omega_v) = G^{(0)}(\underline{k}, \omega_v) V(\underline{p}) \Lambda_{\underline{p}}(\underline{k}, \omega_v) G^{(0)}(\underline{k}-\underline{p}, \omega_v) \quad (57)$$

which is shown graphically in Figure 1. Here  $G^{(0)}(\underline{k}, \omega_v)$  is the Green function of the interacting electron gas and  $\Lambda_{\underline{p}}(\underline{k}, \omega_v)$  is the zero frequency vertex function.<sup>22</sup> The second order term in the band structure energy is then from (56),

$$E_b^{(2)} = \frac{1}{\bar{N}} \lim_{T \rightarrow 0} \frac{1}{\beta} \sum_{\underline{k}, \underline{p}, \nu} |V(\underline{p})|^2 \Lambda_{\underline{p}}(\underline{k}, \omega_{\nu}) G^{(0)}(\underline{k}, \omega_{\nu}) G^{(0)}(\underline{k} - \underline{p}, \omega_{\nu}) \quad (58)$$

which upon transforming to a contour integral gives

$$E_b^{(2)} = \frac{1}{\bar{N}} \sum_{\underline{p}, \underline{k}} |V(\underline{p})|^2 \int_C \Lambda_{\underline{p}}(\underline{k}, \omega) G^{(0)}(\underline{k}, \omega) G^{(0)}(\underline{k} - \underline{p}, \omega) d\omega, \quad (59)$$

where  $C$  is the contour of Figure 2. From the definition of the zero frequency dielectric function of the electron gas<sup>22</sup> we therefore have

$$E_b^{(2)} = \frac{1}{2} \frac{1}{\bar{N}} \sum_{\underline{p}} |V(\underline{p})|^2 \frac{1}{w(\underline{p})} \left[ \frac{1}{\epsilon(\underline{p}, 0; \mu)} - 1 \right] \quad (60)$$

with  $w(\underline{p})$  defined in (7) and  $\mu$  being the exact chemical potential.

The higher order terms in the expansion of  $G$  are, on the other hand, not well known, and the analogues of  $\Lambda_{\underline{p}}(\underline{k}, \omega)$  must be approximated.

We illustrate our approximation by re-calculating (58). Using the spectral resolution of  $G^{(0)}(\underline{p}, \omega)$ , i.e.

$$G^{(0)}(\underline{p}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \frac{A(\underline{p}, \omega')}{\omega - \omega'} \quad (61)$$

we have

$$E_b^{(2)} = \frac{1}{\bar{N}} \lim_{T \rightarrow 0} \frac{1}{\beta} \sum_{\underline{p}, \underline{k}, \nu} \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} |V(\underline{p})|^2 \Lambda_{\underline{p}}(\underline{k}, \omega_{\nu}) \frac{A(\underline{k}, \omega_1)}{\omega_{\nu} - \omega_1} \frac{A(\underline{k} - \underline{p}, \omega_2)}{\omega_{\nu} - \omega_2} \quad (62)$$

which, exploiting a further transformation of the  $\nu$  sum to a contour integral gives two pole contributions,

$$E_b^{(2)} = \frac{1}{N} \lim_{T \rightarrow 0} \sum_{\underline{p}, \underline{k}} \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} |V(\underline{p})|^2 A(\underline{k}, \omega_1) A(\underline{k}-\underline{p}, \omega_2) \cdot \left\{ \frac{\Lambda_{\underline{p}}(\underline{k}, \omega_1)}{\omega_1 - \omega_2} n(\omega_1) + \frac{\Lambda_{\underline{p}}(\underline{k}, \omega_2)}{\omega_2 - \omega_1} n(\omega_2) \right\}, \quad (63)$$

where  $n(\omega) = (e^{\beta(\omega-\mu)} + 1)^{-1}$ . Our first approximation is to make an undamped quasi-particle ansatz for the spectral function, i.e.

$$A(\underline{p}, \omega) = 2\pi \delta(\omega - \mathcal{E}_0(\underline{p}) - \Sigma_1(\underline{p})) \quad (64)$$

with  $\Sigma_1(\underline{p})$  defined to be the real part of the self energy satisfying Dyson's equation  $\mathcal{E}(\underline{p}) = \mathcal{E}_0(\underline{p}) + \Sigma_1(\underline{p}, \mathcal{E}(\underline{p}))$ .

Then (63) becomes,

$$\frac{1}{N} \sum_{\underline{p}, \underline{k}} |V(\underline{p})|^2 \left\{ \frac{\Lambda_{\underline{p}}(\underline{k}, \mathcal{E}_0(\underline{k}) + \Sigma_1(\underline{k})) \theta(\mu - \mathcal{E}_0(\underline{k}) - \Sigma_1(\underline{k}))}{[\mathcal{E}_0(\underline{k}) + \Sigma_1(\underline{k}) - \mathcal{E}_0(\underline{k}-\underline{p}) - \Sigma_1(\underline{k}-\underline{p})]} - \frac{\Lambda_{\underline{p}}(\underline{k}, \mathcal{E}_0(\underline{k}-\underline{p}) + \Sigma_1(\underline{k}-\underline{p})) \theta(\mu - \mathcal{E}_0(\underline{k}-\underline{p}) - \Sigma_1(\underline{k}-\underline{p}))}{[\mathcal{E}_0(\underline{k}) + \Sigma_1(\underline{k}) - \mathcal{E}_0(\underline{k}-\underline{p}) - \Sigma_1(\underline{k}-\underline{p})]} \right\}. \quad (65)$$

Our second approximation is to replace  $\Lambda_{\underline{p}}(\underline{k}, \omega)$  in these expressions by  $\epsilon^{-1}(\underline{p}, \omega, \mu)$ .<sup>23</sup> We then have

$$\frac{1}{N} \sum_{\underline{p}, \underline{k}} |V(\underline{p})|^2 \frac{1}{\epsilon(\underline{p}, \omega, \mu)} \left\{ \frac{\theta(\mu - \mathcal{E}_0(\underline{k}) - \Sigma_1(\underline{k})) - \theta(\mu - \mathcal{E}_0(\underline{k}-\underline{p}) - \Sigma_1(\underline{k}-\underline{p}))}{(\mathcal{E}_0(\underline{k}) - \mathcal{E}_0(\underline{k}-\underline{p})) + (\Sigma_1(\underline{k}) - \Sigma_1(\underline{k}-\underline{p}))} \right\}. \quad (66)$$

Furthermore, we write the chemical potential as

$$\mu = \mu_{eg} + \delta\mu^b, \quad (67)$$

where  $\mu_{eg}$  is the chemical potential of an electron gas of density  $\bar{N}/\Omega$ , i.e.

$$\mu_{eg} = \mathcal{E}_f + \Sigma_1(k_f, \mu_{eg}), \quad (68)$$

with  $k_f^3 = 3\pi^2 \bar{N}/\Omega$  and  $\mathcal{E}_f = \frac{\hbar^2}{2m} k_f^2$  so that (66) becomes

$$\begin{aligned} & \frac{1}{\bar{N}} \sum_{\underline{p}, \underline{k}} |V(\underline{p})|^2 \frac{1}{\epsilon(\underline{p}, o, \mu)} \left\{ \theta(\mathcal{E}_{f+\delta_\mu^b} - \mathcal{E}_o(\underline{k}) - (\Sigma_1(\underline{k}, \mathcal{E}(\underline{k})) - \Sigma_1(k_f, \mu_{eg}))) \right. \\ & \quad \left. - \theta(\mathcal{E}_{f+\delta_\mu^b} - \mathcal{E}_o(\underline{k}-\underline{p}) - (\Sigma_1(\underline{k}-\underline{p}, \mathcal{E}(\underline{k}-\underline{p})) - \Sigma_1(k_f, \mu_{eg}))) \right\} \\ & \quad \cdot \frac{1}{(\mathcal{E}_o(\underline{k}) - \mathcal{E}_o(\underline{k}-\underline{p})) + (\Sigma_1(\underline{k}) - \Sigma_1(\underline{k}-\underline{p})))}. \end{aligned} \quad (69)$$

The final approximation is to neglect differences in self energies. For an electron gas at metallic densities this approximation is fairly well satisfied.<sup>24</sup> Thus the final approximate expression is

$$\frac{1}{\bar{N}} \sum_{\underline{p}, \underline{k}} |V(\underline{p})|^2 \frac{1}{\epsilon(\underline{p}, o, \mu)} \left\{ \frac{\theta(\mathcal{E}_{f+\delta_\mu^b} - \mathcal{E}_o(\underline{k})) - \theta(\mathcal{E}_{f+\delta_\mu^b} - \mathcal{E}_o(\underline{k}-\underline{p}))}{\mathcal{E}_o(\underline{k}) - \mathcal{E}_o(\underline{k}-\underline{p})} \right\} \quad (70)$$

For higher order terms we proceed in the same manner. Denoting the above approximation to  $V(\underline{p})\Lambda_{\underline{p}}$  by a double broken line and by a double wavy line the analogous approximation for the electron-electron interaction, we include the class of diagrams given in Figures 3 and 4. It can be shown that these correspond to a random phase approximation in the sense described by Cohen and Ehrenreich<sup>25</sup> provided one takes  $\epsilon(\underline{p}, o, \mu)$  to be the

Lindhard dielectric function.

We next examine certain complications which appear in fourth and higher orders and which are illustrated by the fourth order diagram of Figure 5. This gives a contribution to the band structure energy

$$\begin{aligned} \frac{2}{\beta} \frac{1}{4} \sum_{\tilde{k}, \tilde{p}, \tilde{q}_1, \tilde{q}_2, \nu} & V(-\tilde{k}) \Lambda_{-\tilde{k}}(\tilde{p}+\tilde{k}, \omega_\nu) G^{(0)}(\tilde{p}, \omega_\nu) V(\tilde{q}_1) \Lambda_{\tilde{q}_1}(\tilde{p}, \omega_\nu) \\ & \cdot G^{(0)}(\tilde{p}+\tilde{q}_1, \omega_\nu) V(\tilde{q}_2) \Lambda_{\tilde{q}_2}(\tilde{p}+\tilde{q}_1, \omega_\nu) G^{(0)}(\tilde{p}+\tilde{q}_1+\tilde{q}_2, \omega_\nu) \\ & V(\tilde{k}-\tilde{q}_1-\tilde{q}_2) \Lambda_{\tilde{k}-\tilde{q}_1-\tilde{q}_2}(\tilde{p}+\tilde{q}_1+\tilde{q}_2, \omega_\nu) G^{(0)}(\tilde{p}+\tilde{k}, \omega_\nu) . \end{aligned} \quad (71)$$

In evaluating the  $\nu$  sum, we perform a contour integration and the possibility of double poles is evident (see Figure 6).

The double pole contribution gives rise from differentiation of the factor  $[e^{\beta(\omega-\mu)}+1]^{-1}$ , to a  $\delta$ -function contribution in the  $T = 0$  limit, i.e.

$$\Delta E = - \sum_{\tilde{k}, \tilde{p}, \tilde{q}} \left| \frac{V(\tilde{k})}{G(\tilde{k})} \right| \left| \frac{2 V(\tilde{q})}{\epsilon(\tilde{q})} \right|^2 \frac{\delta(\mathcal{E}_{\tilde{f}+\delta_{\mu}^b} - \mathcal{E}_o(\tilde{p}))}{(\mathcal{E}_o(\tilde{p}) - \mathcal{E}_o(\tilde{p}+\tilde{k}))(\mathcal{E}_o(\tilde{p}) - \mathcal{E}_o(\tilde{p}+\tilde{q}))} \quad (72)$$

From (B-5) and (B-8) the origin of this term is clear. It arises from an expansion of  $\theta(E_{\tilde{f}} - E(\tilde{k}))$  where  $E(\tilde{k})$  is the eigenvalue of the single electron band structure Hamiltonian.

It is important to note that this expansion is invalid when  $\tilde{k}$  is near a zone plane: In fact  $\Delta E$  of (72) diverges quadratically



there. Although the behavior of these anomalous<sup>26</sup> contributions is general, we can ignore them provided the  $\theta$  functions occurring in the other expressions are modified from  $\theta(\mu^b - \mathcal{E}_o(\underline{k}))$  to  $\theta(\mu^b - E(\underline{k}))$  where  $\mu^b = \mathcal{E}_f + \delta_\mu^b = E_f$  and is the chemical potential one computes in a band structure calculation from<sup>27</sup>

$$\bar{N} = 2 \sum_{\underline{k}} \theta(E_f - E(\underline{k})) . \quad (73)$$

The contributions from (71) not involving  $\delta$ -functions may be shown to give the first three terms of (B-8). The first term of this expression is well-defined, however, the second and third, due to the squared denominator, are divergent when the Fermi sphere is near a zone plane. This divergence is an artifact of the asymptotic nature of the expansion (B-1). In Appendix C we show that a resummation of diagrams leads to a finite result.

Finally we make a remark concerning the electron gas term  $E_o(\mu)$ . This can be calculated from approximate expressions for  $\Xi(\mu)$  (e.g. the Nozières-Pines formula). However, to gain some physical insight we expand  $\Xi_o(\mu) + \mu\bar{N}$  about  $\mu_o = \mu_{eg}$ ,

$$\Xi_o(\mu) + \mu\bar{N} = \bar{N}E_o(\mu_o) + \frac{1}{2} \left( \frac{\partial^2 \Xi_o}{\partial \mu^2} \right) (\delta\mu^b)^2 + \dots, \quad (74)$$

and noting

$$\overline{(\Delta N)^2} = kT \left( \frac{\partial N}{\partial \mu} \right)_{T,V} \quad (75)$$

we see that the right hand side of (74) becomes

$$\bar{N}E_o(\mu_o) - \frac{1}{2kT} \overline{(\Delta N \delta \mu^b)^2} + \dots \quad (76)$$

so that the change in electron gas energy lowers the total energy and is clearly related to the distortion of the spherical Fermi surface of the electron gas into the lattice symmetric Fermi surface of the periodic system. We may also observe that if (50) is written as

$$\Xi(\mu) = \Xi_o(\mu) + \Xi_b(\mu) \quad (77)$$

and expanded to fourth order in the external potential, the following expressions are obtained for internal energy, chemical potential and pressure:

$$E = \left\{ E_o(\mu_o) + E_b^{(2)}(\mu_o) + E_b^{(3)}(\mu_o) + E_b^{(4)}(\mu_o) \right\} \quad (78)$$

$$+ \frac{1}{2} \frac{1}{\Omega_o} K_T (\delta \mu_2)^2 + O(V^5),$$

$$\mu = \mu_o + \delta \mu_2 + \delta \mu_3 + \delta \mu_4 + O(V^5) \quad (79)$$

where

$$\delta \mu_2 = \left\{ E_b^{(2)}(\mu_o) - \frac{r_s}{3} \frac{dE_b^{(2)}}{dr_s}(\mu_o) \right\} \quad (80)$$

$$\delta \mu_3 = \left\{ E_b^{(3)}(\mu_o) - \frac{r_s}{3} \frac{dE_b^{(3)}}{dr_s}(\mu_o) \right\} \quad (81)$$

$$\delta \mu_4 = \left\{ E_b^{(4)}(\mu_o) - \frac{r_s}{3} \frac{dE_b^{(4)}}{dr_s}(\mu_o) \right\}$$

$$\begin{aligned}
 & + \frac{1}{\Omega_o} K_T \delta\mu_2 \frac{1}{9} \left( r_s^2 \frac{d^2 E_b^{(2)}}{dr_s^2} - 2r_s \frac{dE_b^{(2)}}{dr_s} \right) \\
 & + \frac{1}{\Omega_o} K_T (\delta\mu_2)^2 \left( 1 + \frac{r_s}{3} \frac{dB_T}{dr_s} \right), \quad (82)
 \end{aligned}$$

and

$$\begin{aligned}
 p = \{ p_o(\mu_o) + p^{(2)} + p^{(3)} + p^{(4)} \} & + \frac{1}{\Omega_o} K_T \delta\mu_2 \frac{1}{9} \left( r_s^2 \frac{d^2 E_b^{(2)}}{dr_s^2} - 2r_s \frac{dE_b^{(2)}}{dr_s} \right) \\
 & + \frac{1}{2} \frac{1}{\Omega_o} K_T (\delta\mu_2)^2 \left( 1 + \frac{1}{3} \frac{r_s}{B} \frac{dB_T}{dr_s} \right) + O(V^5) \quad (83)
 \end{aligned}$$

where

$$p^{(m)} = - \frac{1}{4\pi r_s^2} \frac{dE_b^{(m)}}{dr_s} (\mu_o). \quad (84)$$

The quantity  $K_T = 1/B_T$  is the isothermal compressibility of the interacting electron gas and as before  $\mu_o$  is the chemical potential of the interacting electron gas, both evaluated at density  $\Omega_o^{-1}$ . (The bracketed terms are to be expected from zero temperature perturbation theory.) We note that the two methods agree to third order but in fourth order differ for the physical reason outlined above (i.e., fermi surface distortion). These differences although small are not negligible as will be shown in the next section.

Recapitulating to this point, we have seen that the theory presented in section III must be modified in several ways. First, the electron gas term in the total energy must be corrected to take into account the shift in chemical potential due to the ions. Secondly, the expressions of section II for

$\chi_n$ , except for the first, must be multiplied by an additional factor of  $\epsilon^{-1}(\underline{k}, 0, \mu)$ . Thirdly, terms such as 4b of Figure 4 must be included in a self-consistent calculation. (These are essentially Hubbard's<sup>3</sup> H diagrams which from his point of view are connected with double counting.) We now turn to a discussion of the magnitude of these various corrections for the particular case of a solid composed of protons arrayed on a Bravais crystal lattice.

## V. ATOMIC HYDROGEN

In this section we present the results of calculations for zero temperature thermodynamic properties of three atomic hydrogen lattices, simple cubic (SC), face centered cubic (FCC), and body centered cubic (BCC). This choice was made partly for convenience of computation, but more importantly because of the relatively large difference in Madelung constant between SC and the other two structures. We shall use the expressions (78) - (83) and proceed order by order.

### A. Electron Gas

We have taken the Nozières-Pines<sup>29</sup> interpolation formula for the ground state energy of the interacting electron gas.

$$E_o(\mu_o) = \frac{3}{5} \left( \frac{9\pi}{4} \right)^{2/3} r_s^{-2} - \frac{3}{2\pi} \left( \frac{9\pi}{4} \right)^{1/3} r_s^{-1} + (-0.115 + 0.031 \ln r_s). \quad (85)$$

In comparison of structures, the magnitude of the structure independent contribution plays no role so that a better approximation is not necessary. In any case, the Nozières-Pines' expression compares very well with more recent forms<sup>30</sup>.

### B. Madelung Energy

The Madelung energy may be written in the form

$$E_M = -A_M/r_s \quad (86)$$

where the Madelung constant  $A_M$  for the three structures is given by<sup>31</sup>: SC: 1.760122, FCC: 1.791749, and BCC: 1.791861.

### C. Second Order Band Structure Energy

We take the Lindhard expression for the dielectric function in the calculation of the terms in the band structure energy:

$$\epsilon(\eta; \mu_o) = 1 + \frac{1}{2\pi} \left( \frac{4}{9\pi} \right)^{1/3} r_s g(\eta) \quad (87)$$

$$g(\eta) = \frac{2}{\eta} \left[ \frac{1-\eta^2}{4\eta} \ln \left| \frac{\eta+1}{\eta-1} \right| + \frac{1}{2} \right]$$

with  $\eta \equiv k/2k_f$ .

Then the second order band structure energy may be written as: (1,2)

$$E_b^{(2)}(\mu_o) = - \frac{1}{6\pi^2} \sum_{\eta \neq 0} \eta^{-2} \frac{g(\eta)}{1 + \frac{1}{2\pi} \left( \frac{4}{9\pi} \right)^{1/3} r_s g(\eta)} \quad (88)$$

### D. Third Order Band Structure Energy

This contribution is given by (B-7) and corresponds to the diagram 3 of Figure 4. It may be written in the following form:

$$E_b^{(3)}(\mu_o) = - \frac{16}{9\pi} \left( \frac{4}{9\pi} \right)^{1/3} r_s \sum_{\eta, \eta_1} \tilde{w}(-\eta) \tilde{w}(\eta - \eta_1) \tilde{w}(\eta_1) H^{(3)}(\eta, \eta_1) \quad (89)$$

where  $\tilde{w}(\eta) = \frac{1}{\eta^2 \epsilon(\eta, \mu_o)}$ , and

$$H^{(3)}(\eta, \eta_1) = k_f \frac{1}{\Omega} \sum_q \frac{n_o(q)}{[\mathcal{E}_o(q) - \mathcal{E}_o(q+k)][\mathcal{E}_o(q) - \mathcal{E}(q+k_1)]} \quad (90)$$

The complete expression for  $H^{(3)}(\eta, \eta_1)$  is given in appendix E.

We note here the following asymptotic properties:

$$H^{(3)}(\eta, \eta_1) \sim \frac{1}{16\pi^2} \frac{1}{\eta\eta_1} \frac{1}{\sqrt{1-\alpha}} \tan^{-1} \sqrt{\frac{1-\alpha}{1+\alpha}} \quad (91)$$

$$\alpha \equiv \hat{\eta} \cdot \hat{\eta}_1, \quad \eta, \eta_1 \ll 1$$

$$H^{(3)}(\eta, \eta_1) \sim \frac{1}{96\pi^2} \frac{1}{\eta^2 \eta_1^2} \left\{ 1 + \frac{1}{5} \left( \frac{1}{\eta^2} + \frac{1}{\eta_1^2} + \frac{1}{\eta\eta_1} \alpha \right) \right\}. \quad (92)$$

$$\eta, \eta_1 \gg 1$$

The third order contribution thus depends linearly on  $r_s$  apart from a weak dependence contained in the dielectric functions.

The function  $H^{(3)}(\eta, \eta_1)$  in this approximation is independent of  $r_s$  and depends purely on the structure. It is everywhere finite but has discontinuous derivatives for certain values

of  $\eta, \eta_1$  as discussed by Lloyd and Sholl<sup>7</sup>. We have expanded  $E_b^{(3)}(\mu_o)$  as a power series in the parameter  $cr_s = -\frac{1}{2\pi} \left( \frac{4}{9\pi} \right)^{1/3} r_s$  which occurs in the Lindhard function,

$$E_b^{(3)}(\mu_o) = ar_s (b_o + cr_s b_1 + (cr_s)^2 b_2 + (cr_s)^3 b_3 + \dots) \quad (93)$$

where  $a = -\frac{16}{9\pi} \left( \frac{4}{9\pi} \right)^{1/3}$ . The values of these structural constants are given in Table I.

#### E. Fourth Order Band Structure Energy

There are several distinct contributions in this order.

We consider first the most divergent parts of the last two terms in (B-8) namely

$$- \frac{2}{N} \sum_{\mathbf{k}} n_o(\mathbf{k}) \sum_{\ell \neq 0} \left| \frac{V(\mathbf{K}_{\ell})}{\epsilon(\mathbf{K}_{\ell})} \right|^4 \frac{1}{(\mathcal{E}_o - \mathcal{E}_{\ell})^3} \quad (94)$$

and

$$- \frac{1}{N} \sum_{\tilde{k}} \sum_{\ell \neq 0} \left| \frac{V(\tilde{K}_{\ell})}{\epsilon(\tilde{K}_{\ell})} \right|^4 \frac{\delta(E_f - \epsilon_o)}{(\epsilon_o - \epsilon_{\ell})^2} \quad (95)$$

which we write as

$$\tilde{E}_4 = \sum_{\ell} \left[ E_1^{(4)}(\tilde{K}_{\ell}) + E_2^{(4)}(\tilde{K}_{\ell}) \right] \quad (96)$$

The explicit expressions for  $E_1$  and  $E_2$  are given by

$$E_1^{(4)}(\eta) = -\frac{3}{8(3\pi)^4} \left( \frac{4}{9\pi} \right)^{2/3} r_s^2 \left[ \frac{1}{\epsilon(\eta)} \right]^4 \cdot \frac{1}{\eta^{10}} \frac{1}{(1-\eta^2)} \left\{ \frac{1-\eta^2}{2\eta} \ln \left| \frac{\eta+1}{\eta-1} \right| + 1 \right\} \quad (97)$$

$$E_2^{(4)}(\eta) = \frac{3}{4} \frac{1}{(3\pi)^4} \left( \frac{4}{9\pi} \right)^{2/3} r_s^2 \left[ \frac{1}{\epsilon(\eta)} \right]^4 \frac{1}{\eta^{10}} \frac{1}{(1-\eta^2)} \quad (98)$$

In Figure 8 we show  $E_1^{(4)}(\eta)/E_2^{(0)}(\eta)$  and  $E_2^{(4)}(\eta)/E_2^{(0)}(\eta)$  as functions of  $\eta$  (where  $E_b^{(2)} = \sum'_{\eta} E_2^{(0)}(\eta)$ ) along with the resummed expression given appendix D. Note that  $E_2^{(4)}(\eta)$  is part of the anomalous contribution as discussed in section IV and that it must be included at finite order to give the appropriate limiting agreement with the resummed diagrams. Furthermore we note from the positions of the first reciprocal lattice vectors that the contribution of this term will be small. The behavior exhibited in this term is representative of the nature of any spurious divergences introduced by zone planes and illustrates the interconnection between band structure



effects and the methods (finite  $T$  and  $T = 0$ ) of perturbation theory.

Secondly, we consider contributions from the diagram 4b of Figure 4. This term may be written

$$E_2^{(4b)} = \frac{64}{27\pi} \left( \frac{4}{9\pi} \right) r_s^3 \sum_{\eta_1} \frac{1}{\eta_1^2 \epsilon(\eta_1)} G^2(\eta_1) \quad (99)$$

where

$$G(\eta_1) = \sum_{\eta_2} \frac{1}{\eta_2^2 \epsilon(\eta_2)} \frac{1}{(\eta_1 - \eta_2)^2 \epsilon(\eta_1 - \eta_2)} \cdot [2H^{(3)}(\eta_1, \eta_2) + H^3(\eta_2, \eta_2 - \eta_1)] \quad (100)$$

and can be calculated readily since the expressions for  $H^{(3)}(\eta_1, \eta_2)$  are known. Furthermore, apart from the weak  $r_s$  dependence of  $\epsilon$  this term is proportional to  $r_s^3$ . Numerical values for two representative values of  $r_s$  are given in Table II.

We next consider the correction which arises as a consequence of the chemical potential shift, namely the last term in (78).

$$E_1^{(4b)} = \frac{1}{2} \frac{1}{\Omega_0} K_T (\delta\mu_2)^2, \quad (101)$$

This is known from the expressions for the compressibility of the electron gas and the second order value of the chemical potential. In fact, as a consequence of the compressibility sum rule, it may be shown that this term is precisely given by the diagram for  $E_2^{(4b)}$  in the limit that the momentum transferred by the internal Coulomb line approaches zero.

Finally we consider contributions due to diagrams of the form labelled 4a in Figure 4. There are two contributions apart from those already discussed in the first part of this section and are given in (B-8). One is an off diagonal part

$$2\Omega_0 \sum_{\substack{i \neq 0, l \\ j \neq 0, l \\ l \neq 0}} \frac{V(\tilde{K}_l)}{\epsilon(\tilde{K}_l)} \frac{V(-\tilde{K}_i)}{\epsilon(\tilde{K}_i)} \frac{V(\tilde{K}_j - \tilde{K}_l)}{\epsilon(\tilde{K}_j - \tilde{K}_l)} \cdot \frac{1}{\Omega} \sum_{\tilde{k}} \frac{n_o(\tilde{k})}{(\epsilon_0 - \epsilon_i)(\epsilon_0 - \epsilon_j)(\epsilon_0 - \epsilon_l)} \quad (102)$$

and the other has diagonal parts:

$$2\Omega_0 \sum_{\substack{i \neq 0, l \\ l \neq 0}} \left| \frac{V(\tilde{K}_l)}{\epsilon(\tilde{K}_l)} \right|^2 \left| \frac{V(\tilde{K}_i)}{\epsilon(\tilde{K}_i)} \right|^2 \sum_{\tilde{k}} n_o(\tilde{k}) \left\{ \frac{1}{(\epsilon_0 - \epsilon_l)^2 (\epsilon_0 - \epsilon_{i-l})} - \frac{1}{(\epsilon_0 - \epsilon_l)^2 (\epsilon_0 - \epsilon_i)} \right\} \quad (103)$$

and

$$- \frac{1}{N} \sum_{\substack{i \neq 0, l \\ l \neq 0}} \left| \frac{V(\tilde{K}_l)}{\epsilon(\tilde{K}_l)} \right|^2 \left| \frac{V(\tilde{K}_i)}{\epsilon(\tilde{K}_i)} \right|^2 \sum_{\tilde{k}} \frac{\delta(E_{\tilde{F}} - \epsilon_0)}{(\epsilon_0 - \epsilon_l)(\epsilon_0 - \epsilon_i)}$$

The second part of (103) is an anomalous contribution, which disappears along with the singularities from the double poles if the resummation of appendix D is used. These terms are awkward to handle in numerical work, although in principle there is no difficulty. [One problem is the time needed to calculate a nine dimensional sum. Another is that the kernel

$$K(\tilde{\eta}_1, \tilde{\eta}_2, \tilde{\eta}_3) = \frac{1}{\Omega} \sum_{\tilde{k}} \frac{n_o(\tilde{k})}{(\epsilon_0 - \epsilon_l)(\epsilon_0 - \epsilon_i)(\epsilon_0 - \epsilon_j)} \quad (104)$$

has, as yet, no analytic representation. We have been able to

reduce it to a two dimensional integral. It has asymptotic expansions which give

$$\begin{aligned}
 K(\eta_1, \eta_2, \eta_3) &\sim -\frac{1}{48\pi^2} \frac{1}{(2k_f)^3} \frac{1}{\eta_1} \frac{1}{\eta_2} \frac{1}{\eta_3} (\eta_1, \eta_2, \eta_3 \gtrsim 1.5) \\
 &\sim -\frac{1}{\eta_1 \eta_2} f(\hat{\eta}_1, \hat{\eta}_2, \hat{\eta}_3) - \frac{1}{\eta_1 \eta_3} f(\hat{\eta}_1, \hat{\eta}_3, \hat{\eta}_2) - \frac{1}{\eta_2 \eta_3} f(\hat{\eta}_2, \hat{\eta}_3, \hat{\eta}_1) \\
 &\qquad \eta_1, \eta_2, \eta_3 \ll 1.
 \end{aligned} \tag{105}$$

where  $f$  is a complicated function of angles. We calculated these terms (102 and 103) by taking as an approximation for  $K(\eta_1, \eta_2, \eta_3)$  its large  $\eta$  expansion and by setting  $\frac{1}{\epsilon(\eta)} = 1$ . The former is an underestimate but note that for the structures we consider  $\eta$  is always  $> 1$ . The latter is an overestimate. The form is then:

$$E^{(4a)} \cong -\frac{1}{4(3\pi)^2} \left(\frac{4}{9\pi}\right)^{2/3} r_s^2 \sum_{\eta_1} \frac{1}{\eta_1} \left\{ \sum_2 \frac{1}{\eta_2} \frac{1}{(\eta_1 - \eta_2)^2} \right\}^2 \equiv r_s c_4 \tag{106}$$

which is proportional to  $r_s^2$  and is probably an underestimate overall. The values for the factor  $c_4$  are given in Table I.].

In Tables III-V, we give the thermodynamic functions  $p, E, G$ , at  $T = 0^\circ K$  calculated to third order in the electron-ion interaction. In Table II, we list the explicit contributions to fourth order at  $r_s = 1.6$  and  $r_s = 1.36$  corresponding to low pressure and 1.9 Mbar respectively.<sup>32</sup> The contribution  $E^{(4a)}$  is an estimate as noted above. Note the approximate cancellation

in the fourth order, and further that at high pressures the SC lattice is predicted to be unstable relative to FCC and BCC.

## VI. DISCUSSION AND CONCLUSIONS

We have given a procedure for calculating the ground state energy of a simple metal and have shown that there are basically four contributions involved, viz. electron gas, static dielectric energy, Madelung, and core exclusion. Furthermore, we have seen that the shift in chemical potential from that of a uniform electron gas must be taken into account in calculations going beyond 2nd order. In particular, we have emphasized that  $T = 0$  time dependent perturbation theory does not give the true ground state when the unperturbed system is taken to have a spherical Fermi surface (a fact first noted by Kohn and Luttinger<sup>17</sup>) and have shown the relationship of this to the deformation of the unperturbed Fermi surface. We have observed that if one expands the free energy uniformly in powers of electron-ion interaction, differences between finite and zero temperature perturbation theory appear only in fourth and higher orders, and furthermore that certain divergences at zone planes can be resolved by resummations.

The preliminary calculations reported here for atomic hydrogen seem to indicate that a happy cancellation may occur in the fourth order, at least for the SC, FCC, and BCC structures, although more detailed calculations are required to be certain of this. The calculations reported have been done using the Lindhard dielectric function. In third and higher orders this

is a very good approximation since the dielectric function occurs as  $1/\epsilon$ . However, in the second order  $\epsilon - 1$  appears. This acts to change the magnitude of the second order contribution slightly but does not affect the energy differences between SC and the two close-packed structures. The use of the Lindhard function, as noted in section III corresponds to a self consistent Hartree (RPA) approximation. We remark that the zero pressure density of the structures studied will be extremely sensitive to the exact fourth order corrections due to the weakness of the minimum in the free energy as seen in Table IV. Also, a third order calculation predicts an instability of the SC structure relative to the two close packed lattices at a pressure of  $\sim 2 - 3$  Mbar. The exact transition pressure is again sensitive to the magnitude of the fourth order corrections. It is clear, however, that such a transition must appear at some pressure, for the band structure corrections depend upon positive powers of  $r_s$  whereas the Madelung term depends inversely upon  $r_s$ . Thus eventually, the static lattice having the lowest Madelung energy should be most stable.

Brovman et al.<sup>10</sup> have computed ground state energies for atomic hydrogen at zero pressure by using the  $T = 0$  expansion to third order in the electron-ion interaction and found an interesting class of low energy anisotropic structures. We

regard the effect of fourth order corrections to these calculations as an open question, but one that can be settled using the above expressions. Finally, we again emphasize that we have treated the lattice as static and that it will be necessary to consider lattice zero point energy in a complete determination of structural stability since the zero point energy is of the magnitude of  $E_b^{(3)}$ . Calculations of such phonon effects are in progress.<sup>33</sup>

### Acknowledgments

We would like to thank Drs. B. Nickel and A. B. Bringer  
for numerous helpful discussions.



## Appendix A.

We derive (29) by writing  $W$  in the form

$$\begin{aligned} \frac{W}{\Omega} = & \sum_{\tilde{k}} K_1(\tilde{k}) V(-\tilde{k}) V(\tilde{k}) + \sum_{\tilde{k}, \tilde{q}} K_2(\tilde{k}, \tilde{q}) V(\tilde{k} + \tilde{q}) V(-\tilde{q}) V(-\tilde{k}) \\ & + \sum_{\tilde{k}, \tilde{q}_1, \tilde{q}_2} K_3(\tilde{k}, \tilde{q}_1, \tilde{q}_2) V(\tilde{k} + \tilde{q}_1 + \tilde{q}_2) V(-\tilde{k}) V(-\tilde{q}_1) V(-\tilde{q}_2) + \dots \end{aligned} \quad (A1)$$

Defining symmetrical coefficients by

$$\begin{aligned} L_1(\tilde{k}) &= [K_1(\tilde{k}) + K_1(-\tilde{k})] \\ L_2(\tilde{k}, \tilde{q}) &= [K_2(\tilde{k}, \tilde{q}) + K_2(-\tilde{k}-\tilde{q}, \tilde{q}) + K_2(\tilde{q}, \tilde{k})] \\ L_3(\tilde{k}, \tilde{q}_1, \tilde{q}_2) &= [K_3(\tilde{k}, \tilde{q}_1, \tilde{q}_2) + K_3(-\tilde{k}-\tilde{q}_1-\tilde{q}_2, \tilde{q}_1, \tilde{q}_2) \\ &\quad + K_3(\tilde{q}_1, \tilde{k}, \tilde{q}_2) + K_3(\tilde{q}_2, \tilde{q}_1, \tilde{k})] \\ &\dots, \end{aligned} \quad (A2)$$

we may write (A1) as

$$\begin{aligned} \frac{W}{\Omega} = & \frac{1}{2} \sum_{\tilde{k}} L_1(\tilde{k}) V(\tilde{k}) V(-\tilde{k}) + \frac{1}{3} \sum_{\tilde{k}, \tilde{q}} L_2(\tilde{k}, \tilde{q}) V(\tilde{k} + \tilde{q}) V(-\tilde{q}) V(-\tilde{k}) \\ & + \frac{1}{4} \sum_{\tilde{k}, \tilde{q}_1, \tilde{q}_2} L_3(\tilde{k}, \tilde{q}_1, \tilde{q}_2) V(\tilde{k} + \tilde{q}_1 + \tilde{q}_2) V(-\tilde{k}) V(-\tilde{q}_1) V(-\tilde{q}_2) + \dots \end{aligned} \quad (A3)$$

Taking the variation of (A3) with respect to  $V(-\tilde{k})$  we have

$$\frac{1}{\Omega} \sum_{\tilde{k}} \frac{\delta W}{\delta V(-\tilde{k})} = \sum_{\tilde{k}} L_1(\tilde{k}) V(\tilde{k}) + \sum_{\tilde{k}, \tilde{q}} L_2(\tilde{k}, \tilde{q}) V(\tilde{k} + \tilde{q}) V(-\tilde{q})$$

$$+ \sum_{\underline{k}, \underline{q}_1, \underline{q}_2} L_3(\underline{k}, \underline{q}_1, \underline{q}_2) V(\underline{k} + \underline{q}_1 + \underline{q}_2) V(-\underline{q}_1) V(-\underline{q}_2) + \dots \quad (\text{A4})$$

Equating (26) and (A4) we have, noting that the V's are arbitrary external potentials,

$$\chi_1 = L_1, \chi_2 = L_2, \dots$$

and hence (29).

## Appendix B.

To derive an expansion of (41) we write the band energy as

$$E(\underline{k}) = \xi_o(\underline{k}) + \sum_i \frac{\tilde{V}_{oi} \tilde{V}_{io}}{\xi_o - \xi_i} + \dots, \quad (B1)$$

and the occupation number as

$$n(\underline{k}) = n_o(\underline{k}) - \delta(E_f - \xi_o(\underline{k})) \cdot \sum_i \frac{\tilde{V}_{oi} \tilde{V}_{io}}{\xi_o - \xi_i} + \dots, \quad (B2)$$

where  $n_o(\underline{k}) = \theta(E_f - \xi_o(\underline{k}))$  and  $n(\underline{k}) = \theta(E_f - E(\underline{k}))$ . Clearly when  $\underline{k}$  is near a zone plane these must be viewed as asymptotic. We find the following expressions for the Fourier components of the density

$$\rho_l^{(1)} = \frac{2}{\Omega} \sum_{\underline{k}} n_o(\underline{k}) \frac{\tilde{V}_{-l0}}{\xi_o - \xi_l} \quad (B3)$$

$$\begin{aligned} \rho_l^{(2)} = \frac{2}{\Omega} \sum_{\underline{k}} n_o(\underline{k}) \left\{ 2 \sum_{i \neq 0, l} \frac{\tilde{V}_{oi} \tilde{V}_{il}}{(\xi_o - \xi_l)(\xi_o - \xi_i)} \right. \\ \left. + \sum_{i \neq 0, l} \frac{\tilde{V}_{il} \tilde{V}_{oi}}{(\xi_o - \xi_{i-l})(\xi_o - \xi_i)} \right\} \quad (B4) \end{aligned}$$

$$\begin{aligned} \rho_l^{(3)} = \frac{2}{\Omega} \sum_{\underline{k}} n_o(\underline{k}) \left\{ 2 \sum_{i, j \neq 0, l} \frac{\tilde{V}_{-li} \tilde{V}_{ij} \tilde{V}_{jo}}{(\xi_o - \xi_i)(\xi_o - \xi_j)(\xi_o - \xi_l)} \right. \\ \left. + 2 \sum_{\substack{i \neq 0, l \\ j \neq 0, i}} \frac{\tilde{V}_{il} \tilde{V}_{oj} \tilde{V}_{ji}}{(\xi_o - \xi_{i-l})(\xi_o - \xi_i)(\xi_o - \xi_j)} \right\} \end{aligned}$$

$$\begin{aligned}
& + 2 \frac{\tilde{V}_{ol}}{(\epsilon_o - \epsilon_l)^2} \sum_{i \neq l, o} \frac{\tilde{V}_{li} \tilde{V}_{il}}{(\epsilon_o - \epsilon_i)} \\
& - 2 \frac{\tilde{V}_{ol}}{(\epsilon_o - \epsilon_l)^2} \sum_{i \neq o} \frac{\tilde{V}_{oi} \tilde{V}_{io}}{(\epsilon_o - \epsilon_i)} \\
& - 2 \frac{\tilde{V}_{ol}}{(\epsilon_o - \epsilon_l)} \sum_{i \neq o} \frac{\tilde{V}_{oi} \tilde{V}_{io}}{(\epsilon_o - \epsilon_i)^2} \} \\
& - \frac{2}{\Omega} \sum_{\tilde{k}} \delta(E_f - \epsilon_o(\tilde{k})) \frac{2\tilde{V}_{ol}}{(\epsilon_o - \epsilon_l)} \sum_{i \neq o} \frac{\tilde{V}_{oi} \tilde{V}_{io}}{(\epsilon_o - \epsilon_i)}
\end{aligned} \tag{B5}$$

Using (29) and supplying the extra factor of  $\epsilon^{-1}(\tilde{k})$  in the third and higher orders, we find for the energy,

$$E_b^{(2)} = \frac{1}{N} \sum_{\tilde{k}, l} |V(\tilde{K}_l)|^2 \frac{1}{\epsilon(\tilde{K}_l)} \frac{2n_o(\tilde{k})}{(\epsilon_o - \epsilon_l)} \tag{B6}$$

$$\begin{aligned}
E_b^{(3)} = \frac{2}{N} \sum_{\tilde{k}} \sum_{\substack{i \neq o, l \\ \tilde{l} \neq o}} n_o(\tilde{k}) & \frac{V(-\tilde{K}_l)}{\epsilon(-\tilde{K}_l)} \frac{V(+\tilde{K}_l - \tilde{K}_i)}{\epsilon(+\tilde{K}_l - \tilde{K}_i)} \frac{V(\tilde{K}_i)}{\epsilon(\tilde{K}_i)} \\
& \cdot \frac{1}{(\epsilon_o - \epsilon_i)(\epsilon_o - \epsilon_l)}
\end{aligned} \tag{B7}$$

$$\begin{aligned}
E_b^{(4a)} = \frac{2}{N} \sum_{\tilde{k}} n_o(\tilde{k}) & \left\{ \sum_{\substack{i \neq o, l \\ j \neq o, l \\ l \neq o}} \frac{V(\tilde{K}_l)}{\epsilon(\tilde{K}_l)} \frac{V(-\tilde{K}_i)}{\epsilon(-\tilde{K}_i)} \frac{V(\tilde{K}_i - \tilde{K}_j)}{\epsilon(\tilde{K}_i - \tilde{K}_j)} \frac{V(\tilde{K}_j - \tilde{K}_l)}{\epsilon(\tilde{K}_j - \tilde{K}_l)} \right. \\
& \cdot \frac{1}{(\epsilon_o - \epsilon_l)(\epsilon_o - \epsilon_i)(\epsilon_o - \epsilon_j)}
\end{aligned}$$

$$\begin{aligned}
 & + \sum_{\substack{i \neq 0 \\ i \neq 0, l}} \left| \frac{V(\tilde{K}_l)}{\epsilon(\tilde{K}_l)} \right|^2 \left| \frac{V(\tilde{K}_i - \tilde{K}_l)}{\epsilon(\tilde{K}_i - \tilde{K}_l)} \right|^2 \cdot \frac{1}{(\epsilon_0 - \epsilon_l)^2 (\epsilon_0 - \epsilon_i)} \\
 & - \left. \sum_{\substack{l \neq 0 \\ i \neq 0}} \left| \frac{V(\tilde{K}_l)}{\epsilon(\tilde{K}_l)} \right|^2 \left| \frac{V(\tilde{K}_i)}{\epsilon(\tilde{K}_i)} \right|^2 \cdot \frac{1}{(\epsilon_0 - \epsilon_l)^2 (\epsilon_0 - \epsilon_i)} \right\} \\
 & - \frac{1}{N} \sum_{\substack{k \\ \sim}} \sum_{\substack{i \neq 0 \\ l \neq 0}} \left| \frac{V(\tilde{K}_l)}{\epsilon(\tilde{K}_l)} \right|^2 \left| \frac{V(\tilde{K}_i)}{\epsilon(\tilde{K}_i)} \right|^2 \cdot \frac{\delta(E_f - \epsilon_0)}{(\epsilon_0 - \epsilon_l)(\epsilon_0 - \epsilon_i)} \quad . \quad (B8)
 \end{aligned}$$

### Appendix C.

The diagrams which correspond to the second and third terms of (B8) are shown in Figure 6. The two diagrams of 6a are equal in magnitude when summed over  $\underline{k}, \underline{q}$  so we need only calculate one and multiply the result by a factor of 2. We now observe that the series of Figure 7a may be summed, i.e.

$$\begin{aligned}
 & G_o(\underline{p}, \omega_v) \sum_{m=1}^{\infty} [|\lambda \tilde{v}_{\underline{k}}|^2 G_o(\underline{p}+\underline{k}, \omega_v) G_o(\underline{p}, \omega_v)]^m \\
 &= G_o(\underline{p}, \omega_v) \left[ \frac{1}{1 - \lambda^2 |\tilde{v}_{\underline{k}}|^2 G_o(\underline{p}+\underline{k}, \omega_v) G_o(\underline{p}, \omega_v)} - 1 \right] \quad (C1)
 \end{aligned}$$

Hence the series of Figure 7b can also be summed, and supplying the factor of 2, the resummation gives for Figure 6a,

$$\begin{aligned}
 & \frac{4}{N} \sum_{\substack{\underline{k} \neq \underline{q} \\ \underline{p}, \underline{v}}} |\tilde{v}_{\underline{k}}|^2 |\tilde{v}_{\underline{q}}|^2 \int_0^1 \lambda^3 d\lambda \frac{1}{G_o^{-1}(\underline{p}, \omega_v) G_o^{-1}(\underline{p}+\underline{k}, \omega_v) - \lambda^2 |\tilde{v}_{\underline{k}}|^2} \\
 & \quad \cdot \frac{1}{G_o^{-1}(\underline{p}, \omega_v) G_o^{-1}(\underline{p}+\underline{q}, \omega_v) - \lambda^2 |\tilde{v}_{\underline{q}}|^2}, \quad (C2)
 \end{aligned}$$

which no longer has double poles and hence is always finite.

Similarly, the contribution of Figure 6b is the first term in the series of Figure 7c which may be summed to give,

$$\begin{aligned}
 & \frac{1}{N} \sum_{\underline{p}, \underline{k}, \underline{v}} |\tilde{v}_{\underline{k}}|^2 \int_0^1 d(\lambda^2) \left\{ \frac{1}{G_o^{-1}(\underline{p}, \omega_v) G_o^{-1}(\underline{p}+\underline{k}, \omega_v) - \lambda^2 |\tilde{v}_{\underline{k}}|^2} \right. \\
 & \quad \left. - G_o(\underline{p}, \omega_v) G_o(\underline{p}+\underline{k}, \omega_v) \right\}. \quad (C3)
 \end{aligned}$$

This again has only simple poles, and moreover is seen to be a correction to  $E_b^{(2)}$  rather  $E_b^{(4)}$ . In fact, the integrals appearing in (C3) can be done analytically.

## Appendix D.

We give an explicit expression for (C3) by noting that the roots of the equation

$$G_o^{-1}(\underline{p}, \omega) G_o^{-1}(\underline{p} + \underline{k}, \omega) - \lambda^2 |\tilde{v}_{\underline{k}}|^2 = 0 \quad (D1)$$

are given by

$$\tilde{\omega}_{\pm} = \frac{1}{2} \left\{ (\mathcal{E}(\underline{p}) + \mathcal{E}(\underline{p} - \underline{k})) \pm [(\mathcal{E}(\underline{p} - \underline{k}) - \mathcal{E}(\underline{p}))^2 + 4\lambda^2 |\tilde{v}_{\underline{k}}|^2]^{\frac{1}{2}} \right\}, \quad (D2)$$

where  $\mathcal{E}(\underline{p}) = \mathcal{E}_o(\underline{p}) + \Sigma_1(\underline{p})$  as in (64). Then (C3) becomes

$$\frac{1}{N} \sum_{\underline{k}} |\tilde{v}_{\underline{k}}|^2 \int_0^1 d(\lambda^2) \sum_{\underline{p}} \left\{ \frac{\theta(\mu^b - \omega_-)}{\omega_- - \omega_+} - \frac{\theta(\mu^b - \omega_+)}{\omega_- - \omega_+} - \frac{2\theta(\mu^b - \mathcal{E}_o(\underline{p}))}{\mathcal{E}_o(\underline{p}) - \mathcal{E}_o(\underline{p} - \underline{k})} \right\} \quad (D3)$$

with

$$\omega_{\pm} = \frac{1}{2} \left\{ (\mathcal{E}_o(\underline{p}) + \mathcal{E}_o(\underline{p} - \underline{k})) \pm [(\mathcal{E}_o(\underline{p} - \underline{k}) - \mathcal{E}_o(\underline{p}))^2 + 4\lambda^2 |\tilde{v}_{\underline{k}}|^2]^{\frac{1}{2}} \right\} \quad (D4)$$

and where we have assumed the self energy to be momentum independent as discussed in section III. We rewrite (D3) as

$$\sum_{\underline{k}} [E_4(\underline{k}) - E_4^{(o)}(\underline{k})] \quad (D5)$$

where  $E_4(\underline{k})$  is given by the first two terms and  $E_4^{(o)}(\underline{k})$  by the last. Then in terms of the dimensionless variables:

$$\eta_o = \frac{k}{2k_f} \quad v = \frac{\tilde{v}_{\underline{k}}}{\left(\frac{k}{2}\right)^2} \quad \mathcal{E} = \frac{\mu^b}{\left(\frac{k}{2}\right)^2} \quad (D6)$$

$$\Delta = \frac{1}{2} [4\mathcal{E} + v^2]^{\frac{1}{2}}$$

The integrals may be evaluated and we find for  $E_4(\underline{k})$



$$(1) \quad \mathcal{E} < 1 - v$$

$$\begin{aligned} E_4(\tilde{k}) = & - \frac{3}{4} \left( \frac{9\pi}{4} \right)^{2/3} \frac{\eta_0^5}{r_s^2} \left\{ \frac{1}{4} (3\mathcal{E} - 4 + \Delta^2) \frac{v^2}{4} \ln \left| \frac{[\mathcal{E} + 1 + 2\Delta]^{\frac{1}{2}} + \Delta + 1}{[\mathcal{E} + 1 - 2\Delta]^{\frac{1}{2}} - \Delta + 1} \right| \right. \\ & + [\mathcal{E} + 1 + 2\Delta]^{\frac{1}{2}} \left[ \frac{(1+\Delta)}{4} [3\mathcal{E} - 4 + \Delta^2 - 2(1+\Delta)^2] + \frac{4}{3} (\mathcal{E} + 1 + 2\Delta) \right. \\ & \left. \left. + \frac{4}{15} (\mathcal{E} + 1 + 2\Delta) (\mathcal{E} + 1 - 3\Delta) + 4(\Delta^2 - \mathcal{E}) \right] \right. \\ & - [\mathcal{E} + 1 - 2\Delta]^{\frac{1}{2}} \left[ \frac{(1-\Delta)}{4} [3\mathcal{E} - 4 + \Delta^2 - 2(1-\Delta)^2] + \frac{4}{3} (\mathcal{E} + 1 - 2\Delta) \right. \\ & \left. \left. + \frac{4}{15} (\mathcal{E} + 1 - 2\Delta) (\mathcal{E} + 1 + 3\Delta) + 4(\Delta^2 - \mathcal{E}) \right] - \frac{8}{15} \mathcal{E}^{5/2} \right\}, \quad (D7) \end{aligned}$$

$$(2) \quad \mathcal{E} > 1 - v; \quad \mathcal{E} < 1 + v$$

$$\begin{aligned} E_4(\tilde{k}) = & - \frac{3}{4} \left( \frac{9\pi}{4} \right)^{2/3} \frac{\eta_0^5}{r_s^2} \left\{ \frac{1}{4} (3\mathcal{E} - 4 + \Delta^2) \frac{v^2}{4} \ln \left| \frac{[\mathcal{E} + 1 + 2\Delta]^{\frac{1}{2}} + \Delta + 1}{[\Delta^2 - \mathcal{E}]^{\frac{1}{2}}} \right| \right. \\ & + [\mathcal{E} + 1 + 2\Delta]^{\frac{1}{2}} \left[ \frac{(1+\Delta)}{4} (3\mathcal{E} - 4 + \Delta^2 - 2(1+\Delta)^2) + \frac{4}{3} (\mathcal{E} + 1 + 2\Delta) \right. \\ & \left. \left. + \frac{4}{15} (\mathcal{E} + 1 + 2\Delta) (\mathcal{E} + 1 - 3\Delta) + 4(\Delta^2 - \mathcal{E}) \right] - \frac{8}{15} \mathcal{E}^{5/2} \right\} \quad (D8) \end{aligned}$$

$$(3) \quad \mathcal{E} > 1 + v$$

$$\begin{aligned} E_4(\tilde{k}) = & - \frac{3}{4} \left( \frac{9\pi}{4} \right)^{2/3} \frac{\eta_0^5}{r_s^2} \left\{ \frac{1}{4} (3\mathcal{E} - 4 + \Delta^2) \frac{v^2}{4} \ln \left| \frac{[\mathcal{E} + 1 + 2\Delta]^{\frac{1}{2}} + \Delta + 1}{[\mathcal{E} + 1 - 2\Delta]^{\frac{1}{2}} + \Delta - 1} \right| \right. \\ & + [\mathcal{E} + 1 + 2\Delta]^{\frac{1}{2}} \left[ \frac{(\Delta + 1)}{4} [3\mathcal{E} - 4 + \Delta^2 - 2(\Delta + 1)^2] + \frac{4}{3} (\mathcal{E} + 1 + 2\Delta) \right. \\ & \left. \left. + \frac{4}{15} (\mathcal{E} + 1 + 2\Delta) (\mathcal{E} + 1 - 3\Delta) + 4(\Delta^2 - \mathcal{E}) \right] \right\} \end{aligned}$$

$$\begin{aligned}
 & - [\xi+1-2\Delta]^{\frac{1}{2}} \left[ \frac{(\Delta-1)}{4} [3\xi-4+\Delta^2-2(\Delta-1)^2] - \frac{4}{3} (\xi+1-2\Delta) \right. \\
 & \left. - \frac{4}{15} (\xi+1-2\Delta) (\xi+1+3\Delta) - 4(\Delta^2-\xi) \right] - \frac{8}{15} \xi^{5/2} \} \quad (D9)
 \end{aligned}$$

and for  $E_4^{(o)}(\tilde{k})$

$$E_4^{(o)}(\tilde{k}) = - \frac{3}{16} \left( \frac{9\pi}{4} \right)^{2/3} \frac{\eta_o^5}{r_s^2} v^2 \left\{ (\xi-1) \ln \left| \frac{\sqrt{\xi}+1}{\sqrt{\xi}-1} \right| + 2\sqrt{\xi} \right\} . \quad (D10)$$

To see the relative magnitude of these contributions we compare them with the second order contribution which we write as

$$E_b^{(2)} = \sum_{\tilde{k}} E_2(\tilde{k}) . \quad (D11)$$

We distinguish between the cases in which  $E_2$  is evaluated using  $\epsilon(\tilde{k}, \mu_o)$  and  $\epsilon(\tilde{k}, \mu)$  by  $E_2^{(o)}$  and  $E_2$ , where the  $\mu$  dependent Lindhard function  $\epsilon(\tilde{k}, \mu)$  is given by

$$\epsilon(\tilde{k}, \mu) = 1 + \frac{r_s}{2\pi \left( \frac{9\pi}{4} \right)^{1/3}} \frac{1}{\eta_o \eta} \left[ \frac{1-\eta^2}{2\eta} \ln \left| \frac{\eta+1}{\eta-1} \right| + 1 \right] \quad (D12)$$

with

$$\eta_o = \frac{k}{2k_f} \quad \eta = \frac{k}{2\sqrt{\mu} b} .$$

In Figure 8 we show  $[E_4(\eta) - E_4^{(o)}(\eta)]/E_2^{(o)}(\eta)$  with  $\mu = \mu_o$ .

## Appendix E.

The function (90) was originally evaluated by Lloyd and Sholl<sup>8</sup>. We write it in a somewhat different form:

$$\begin{aligned}
 H^{(3)}(\eta_1, \eta_2) = & \frac{1}{64\pi^2} \frac{1}{\eta_1 \eta_2 \sin^2 \theta} \operatorname{Re} \left\{ (\eta_1 - \eta_2 \cos \theta) \log \left( \frac{\eta_2 + 1}{\eta_2 - 1} \right) \right. \\
 & + (\eta_2 - \eta_1 \cos \theta) \log \left( \frac{\eta_1 + 1}{\eta_1 - 1} \right) + \beta \log [(\eta_1^2 - 1)(\eta_2^2 - 1)] \\
 & \left. - \beta \log \left\{ [\eta_1^2 \eta_2^2 + \eta_1^2 + \eta_2^2 - 4\eta_1 \eta_2 \cos \theta + \cos 2\theta] + 2\beta(\eta_1 \eta_2 - \cos \theta) \right\} \right\} \quad (E1)
 \end{aligned}$$

where

$$\beta = (\eta_1^2 + \eta_2^2 - 2\eta_1 \eta_2 \cos \theta - \sin^2 \theta)^{\frac{1}{2}}$$

When  $\beta = i\beta'$ , i.e. when  $\eta_1, \eta_2, \eta_1 - \eta_2$  form a triangle inscribed in a circle of diameter 1 this function becomes

$$\begin{aligned}
 & \frac{1}{64\pi^2} \frac{1}{\eta_1 \eta_2 \sin^2 \theta} \left\{ (\eta_1 - \eta_2 \cos \theta) \log \left| \frac{\eta_2 + 1}{\eta_2 - 1} \right| + (\eta_2 - \eta_1 \cos \theta) \log \left| \frac{\eta_1 + 1}{\eta_1 - 1} \right| \right. \\
 & \left. + \beta' \arg [\eta_1^2 \eta_2^2 + \eta_1^2 + \eta_2^2 - 4\eta_1 \eta_2 \cos \theta + \cos 2\theta] + 2\beta' (\eta_1 \eta_2 - \cos \theta) \right\}
 \end{aligned}$$

with  $\beta' = (\sin^2 \theta - \eta_1^2 - \eta_2^2 + 2\eta_1 \eta_2 \cos \theta)^{\frac{1}{2}}$  and the argument function is the principal branch with the branch cut along the positive real axis.

## References

- \* Work supported in part by NASA, contract #NGR-33-010-188, and by the National Science Foundation, contract #GH-33637, through the facilities of the Materials Science Center at Cornell University, Report #1943.
1. N. W. Ashcroft and D. C. Langreth, Phys. Rev. 155, 682 (1967).
  2. V. Heine and D. Weaire, Solid State Phys. 24, (1970).
  3. J. Hubbard, Proc. Roy. Soc. (London) A243, 336 (1958); *ibid.* A244, 199 (1958).
  4. M. H. Cohen, Phys. Rev. 130, 1301 (1963).
  5. P. Nozières and D. Pines, Nuovo Cimento [X] 9, 470 (1958).
  6. E. G. Brovman and Yu. Kagan, Sov. Phys.-JETP 30, 721 (1970) and references therein.
  7. P. Lloyd and C. A. Sholl, J. Phys. C. ser. 2, Vol. 1, 1620 (1968).
  8. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
  9. W. A. Harrison, to be published.
  10. E. G. Brovman, Yu Kagan, and A. Kholas, Sov. Phys.-JETP 34, 1300 (1972).
  11. N. W. Ashcroft and J. Hammerberg, to be published.
  12. The arguments below are to be interpreted in the sense of an implied thermodynamic limit, that is,  $N, \Omega \rightarrow \infty$ ,  $N/\Omega = \text{const.}$  Thus, for example, we may replace  $\frac{N(N-1)}{\Omega^2}$  by  $\left(\frac{N}{\Omega}\right)^2$ .

13. Many pseudopotentials may be so characterized, see e.g. N. W. Ashcroft, Phys. Letters 23, 48 (1966).
14. By "core" we mean to allude to the deviation of the pseudopotential from a pure Coulombic form in the core region due to the pseudopotential transformation and not to imply any other effect of core levels on the energy.
15. See, for example, J. D. Jackson, Classical Electrodynamics (J. Wiley & Sons, Inc., New York 1962), p. 123. We note that the induction is understood to be at fixed total charge so that (25) is the appropriate expression.
16. This terminology is frequently reserved for the first member of the sum.
17. W. Kohn and J. M. Luttinger, Phys. Rev. 118, 41 (1960).
18. J. M. Luttinger and J. C. Ward, Phys. Rev. 118, 1417 (1960).
19. P. C. Martin and J. Schwinger, Phys. Rev. 115, 1342 (1959).
20. This follows directly from differentiation of  $\Xi = -\frac{1}{\beta} \ln \text{Tr } e^{-\beta(H(\lambda) - \mu N)}$ . See also L. D. Landau and E. M. Lifshitz, Statistical Physics (Addison-Wesley, Reading 1969), p. 46.
21. The linear term vanishes since  $G^{(0)}(\underline{k}, \underline{k}-\underline{p}; \omega_{\underline{v}}) = G^{(0)}(\underline{k}, \underline{k}-\underline{p}; \omega_{\underline{v}}) \delta(\underline{k}-\underline{k}+\underline{p})$  and  $V(0) \equiv 0$ .
22. See D. C. Langreth, Phys. Rev. 181, 753 (1969).
23. Thus we essentially ignore vertex corrections to  $\epsilon^{-1}$ .
24. See e.g. L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

25. H. Ehrenreich and M. H. Cohen, Phys. Rev. 115, 786 (1959).
26. See reference 17.
27. This follows by assuming the exact quasi-particle energies to be  $\tilde{\epsilon}(\underline{k}) = E(\underline{k}) + \Sigma_1(\underline{k}, \tilde{\epsilon}(\underline{k}))$  and using the Luttinger<sup>28</sup> formula,  $\bar{N} = 2 \sum_{\underline{k}} \theta(\mu - \tilde{\epsilon}(\underline{k}))$  together with the above approximations for the self energy.
28. J. M. Luttinger, Phys. Rev. 119, 1153 (1960).
29. We use atomic units  $\hbar = \frac{e^2}{2} = 2m = 1$ .
30. P. Vashishta and K. S. Singwi, Phys. Rev. B 6, 875 (1972).
31. C. A. Sholl, Proc. Phys. Soc. (London) 92, 434 (1967).
32. For comparison we have calculated the energy to second

order for the liquid metal from

$$E = E_{eg} + \frac{4k_f^0}{\pi} \int_0^\infty dy \left[ \frac{S_L(g)}{\epsilon_H(g)} - 1 \right]$$

where  $S_L$  is the hard sphere Percus-Yevick structure factor and  $\epsilon_H$  is the Hubbard dielectric function modified to satisfy the compressibility sum rule. For  $r_s = 1.6$  and  $\bar{\eta} =$  packing fraction = .45 we find  $E = -.976$ , these results being very insensitive to  $\bar{\eta}$  ( $\sim 2\%$  for  $\bar{\eta} \sim .7 \rightarrow .3$ ). Most of this change can be traced to the Madelung energy.

33. A correct evaluation of the phonon spectrum is essential in determining the zero pressure density for a given structure, as well as in assessing dynamic stability. Furthermore, only when the presence of phonons is taken into proper account can the virial theorem ( $E = -K + 3p\Omega$ ,

where  $K$  is the kinetic energy of electrons and ions)  
be satisfied.

### Table Captions

- Table I: Parameters in expansion (93) of third order band structure energy.
- Table II: Contributions to fourth order in electron-ion interaction to free energy.  $E_2^{(4b)}$  - Fig. 4b,  $E^{4a}$  - Fig. 4a,  $\tilde{E}_4$  - Fig. 7c,  $E_1^{(4b)}$  - chemical potential correction - see text of Section IV.
- Table III:  $T = 0^\circ\text{K}$  equation of state for atomic hydrogen (to third order). Note that these results are appropriate to a static lattice and do not, therefore, include phonon contributions to the equation of state.
- Table IV: Free energy at  $T = 0^\circ\text{K}$  for atomic hydrogen vs.  $r_s$  (to third order).
- Table V: Gibbs free energy at  $T = 0^\circ\text{K}$  vs. pressure for atomic hydrogen (to third order).



Table I

Lattice (real space)	$b_o$	$b_1$	$b_2$	$b_3$	$c_4$
SC	.08202	.1195	.1506	.1748	-.00310
BCC	.06483	.06591	.05467	.04050	-.00275
FCC	.06663	.06945	.05933	.04555	-.00260

Table II

$r_s = 1.6$				$r_s = 1.36$			
	SC	FCC	BCC	SC	FCC	BCC	
$E_O$	0.190106	-----	-----	0.415590	-----	-----	
$E_M$	-1.100076	-1.119843	-1.119913	-1.294207	-1.317462	-1.317545	
$E_2$	-0.105351	-0.086230	-0.085549	-0.106694	-0.086949	-0.086237	
$E_3$	-0.03227	-0.02753	-0.02687	-0.02815	-0.02385	-0.02327	
$E_1^{4b}$	0.00844	0.00555	0.005459	0.00587	0.003832	0.003765	
$E_2^{4b}$	0.00108	0.00076	0.000762	0.000696	0.000482	0.000485	
$E_4$	-0.00187	-0.000454	-0.000385	-0.00170	-0.000339	-0.000287	
$E_4^{4a}$	-0.0077	-0.0067	-0.0044	-0.0055	-0.0048	-0.0037	

Table III

$r_s$	pressure		
	SC	FCC	BCC
1.65	$-2.03 \times 10^{-4}$	$-5.16 \times 10^{-4}$	$-5.23 \times 10^{-4}$
1.60	7.89	4.31	4.24
1.55	$2.13 \times 10^{-3}$	$1.72 \times 10^{-3}$	$1.71 \times 10^{-3}$
1.50	3.92	3.45	3.44
1.45	6.32	5.78	5.77
1.40	9.54	8.91	8.90
1.35	$1.38 \times 10^{-2}$	$1.31 \times 10^{-2}$	$1.31 \times 10^{-2}$
1.30	1.96	1.88	1.87
1.25	2.74	2.64	2.64
1.20	3.79	3.67	3.67
1.15	5.22	5.08	5.08
1.10	7.19	7.02	7.02
1.05	9.92	9.71	9.71
1.00	$1.37 \times 10^{-1}$	$1.35 \times 10^{-1}$	$1.35 \times 10^{-1}$

NOTE: 1 unit of pressure = 147.15 Mbar

Table IV

$r_s$	free energy		
	SC	FCC	BCC
1.65	-1.04803	-1.04338	-1.04209
1.64	-1.04807	-1.04353	-1.04224
1.63	-1.04805	-1.04361	-1.04233
1.62	-1.04796	-1.04363	-1.04236
1.61	-1.04781	-1.04360	-1.04233
1.60	-1.04759	-1.04345	-1.04222
1.55	-1.04538	-1.04188	-1.04062
1.50	-1.04104	-1.03818	-1.03693
1.45	-1.03414	-1.03197	-1.03073
1.40	-1.02414	-1.02272	-1.02149
1.35	-1.01042	-1.00979	-1.00858
1.30	-0.99217	-0.99242	-0.99122
1.25	-0.96842	-0.96961	-0.96843
1.20	-0.93796	-0.94019	-0.93902
1.15	-0.89928	-0.90262	-0.90147
1.10	-0.85045	-0.85502	-0.85388
1.05	-0.78903	-0.79495	-0.79383
1.00	-0.71188	-0.71929	-0.71819

Table V

pressure	Gibbs free energy		
	SC	FCC	BCC
0.0	-1.0481	-1.0436	-1.0424
$5.0 \times 10^{-4}$	-1.0390	-1.0349	-1.0336
$1.0 \times 10^{-3}$	-1.0305	-1.0266	-1.0253
5.	-0.9707	-0.9683	-0.9670
$1.0 \times 10^{-2}$	-0.9092	-0.9080	-0.9068
2.	-0.8081	-0.8085	-0.8073
3.	-0.7233	-0.7248	-0.7237
5.	-0.5809	-0.5841	-0.5829
$1.0 \times 10^{-1}$	-0.3019	-0.3085	-0.3075
5.	-0.9707	-0.9683	-0.9670
1.0	1.8572	1.8377	1.8387
5.0	5.6614	5.6273	5.6282

## Figure Captions

- Figure 1: First order correction to the Green Function. The solid line represents the electron gas Green function, the dashed line the bare external potential, and the triangle the vertex function of the electron gas.
- Figure 2: Integration contour for (59).
- Figure 3: Corrections to the Green function. The double dashed line and double wavy line represent the dielectric approximation to the vertex function described in the text.
- Figure 4: Contributions to the band structure energy.
- Figure 5: Fourth order contribution to the band structure energy given by (71).
- Figure 6: Divergent fourth order diagrams.
- Figure 7: (a) Partial summation for Green function.  
 (b) Partial summation for the diagrams of 6a.  
 (c) Partial summation for the diagrams of 6b.
- Figure 8:  $\text{_____} \quad [E_4(\eta) - E_4^{(o)}(\eta)]/E_2^{(o)}(\eta) \quad (\text{cf. Appendix D}).$   
 $\text{-----} \quad E_1^{(4)}(\eta)/E_2^{(o)}(\eta)$   
 $\text{.....} \quad [E_1^{(4)}(\eta) + E_2^{(4)}(\eta)]/E_2^{(o)}(\eta) \quad (\text{cf. (97)}$   
 $\text{and (98) and Appendix D}).$   
 Note that left hand axis is  $\frac{1}{\eta}$ ; right hand is  $\eta$ .
- Figure 9: Gibbs free energy difference relative to the simple cubic lattice for FCC and BCC metallic hydrogen.

$$= = \frac{\begin{array}{c} V(\underline{p}) \\ \times \\ \vdots \\ \triangle \\ \underline{k}, \omega_{\nu} \quad \underline{k} - \underline{p}, \omega_{\nu} \end{array}}{\Lambda_{\underline{p}}(\underline{k}, \omega_{\nu})}$$

Fig. 1

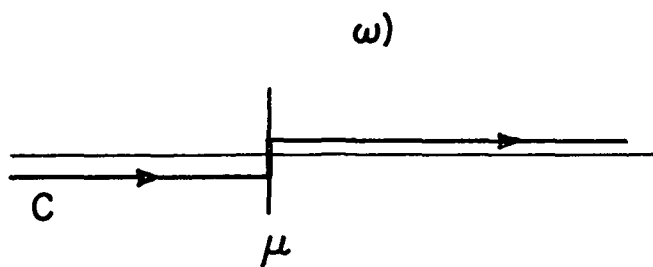


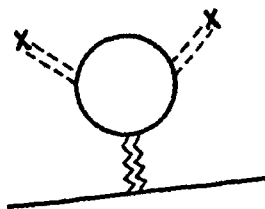
Fig. 2

Order                      Green function

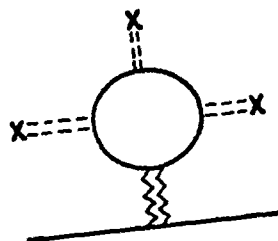
1



2



3a



3b

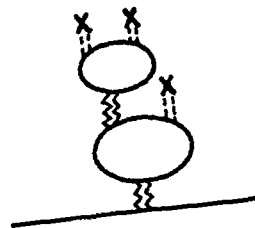
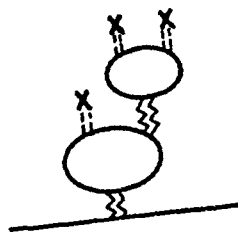


Fig. 3




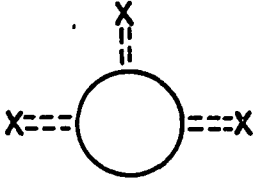
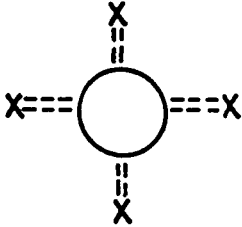
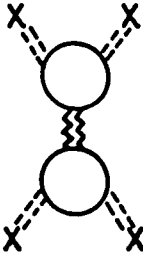
<u>Order</u>	<u><math>E_b^{(n)}</math></u>
2	
3	
4a	
4b	 <span style="margin-left: 20px;">(2)</span>

Fig. 4

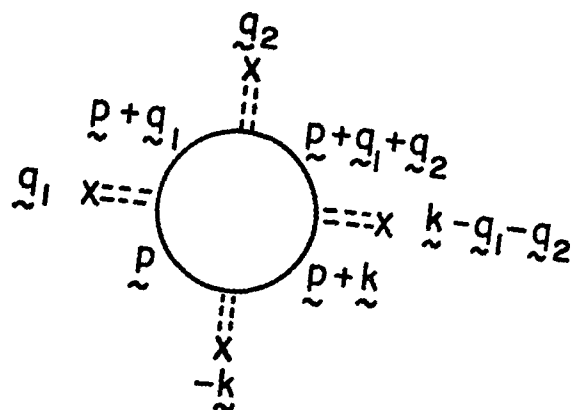
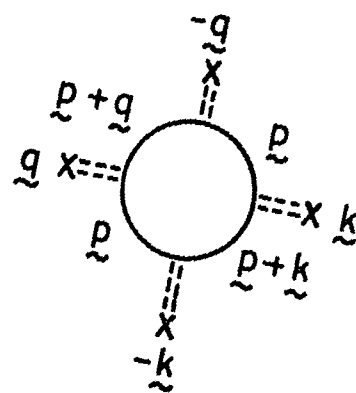
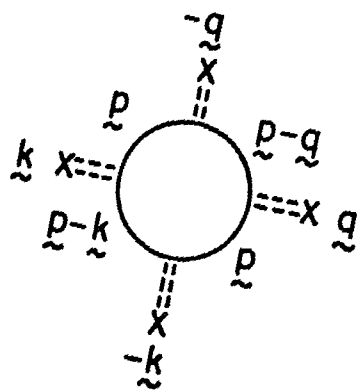


Fig. 5

6a



6b

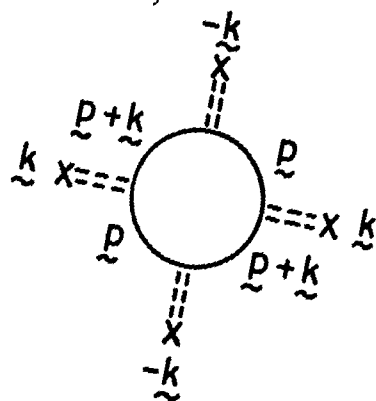


Fig. 6

7a

$$\frac{\begin{array}{c} -k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} +k \\ \text{---} \\ \text{---} \\ \text{---} \end{array}}{\begin{array}{ccc} p & p+k & p \end{array}} + \frac{\begin{array}{c} -k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} -k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} k \\ \text{---} \\ \text{---} \\ \text{---} \end{array}}{\begin{array}{ccccc} p & p+k & p & p+k & p \end{array}} + \dots$$

7b

$$\begin{array}{c} k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} -q \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \begin{array}{c} -k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} -k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} q \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} -q \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \begin{array}{c} k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} -k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} q \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} -q \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \dots$$

7c

$$\begin{array}{c} -k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \begin{array}{c} -k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} -k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} \begin{array}{c} -k \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \dots$$

Fig. 7

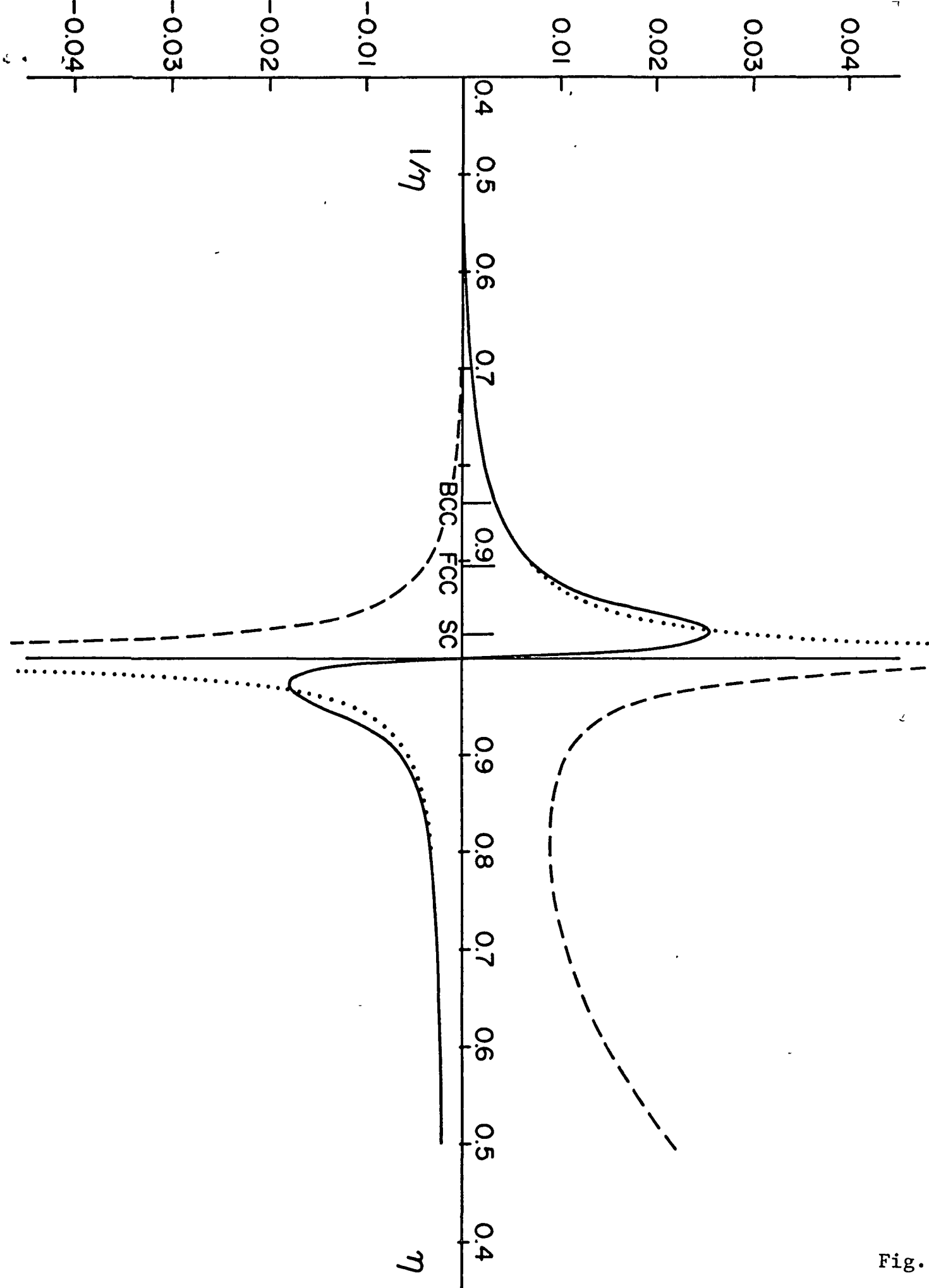


Fig. 8

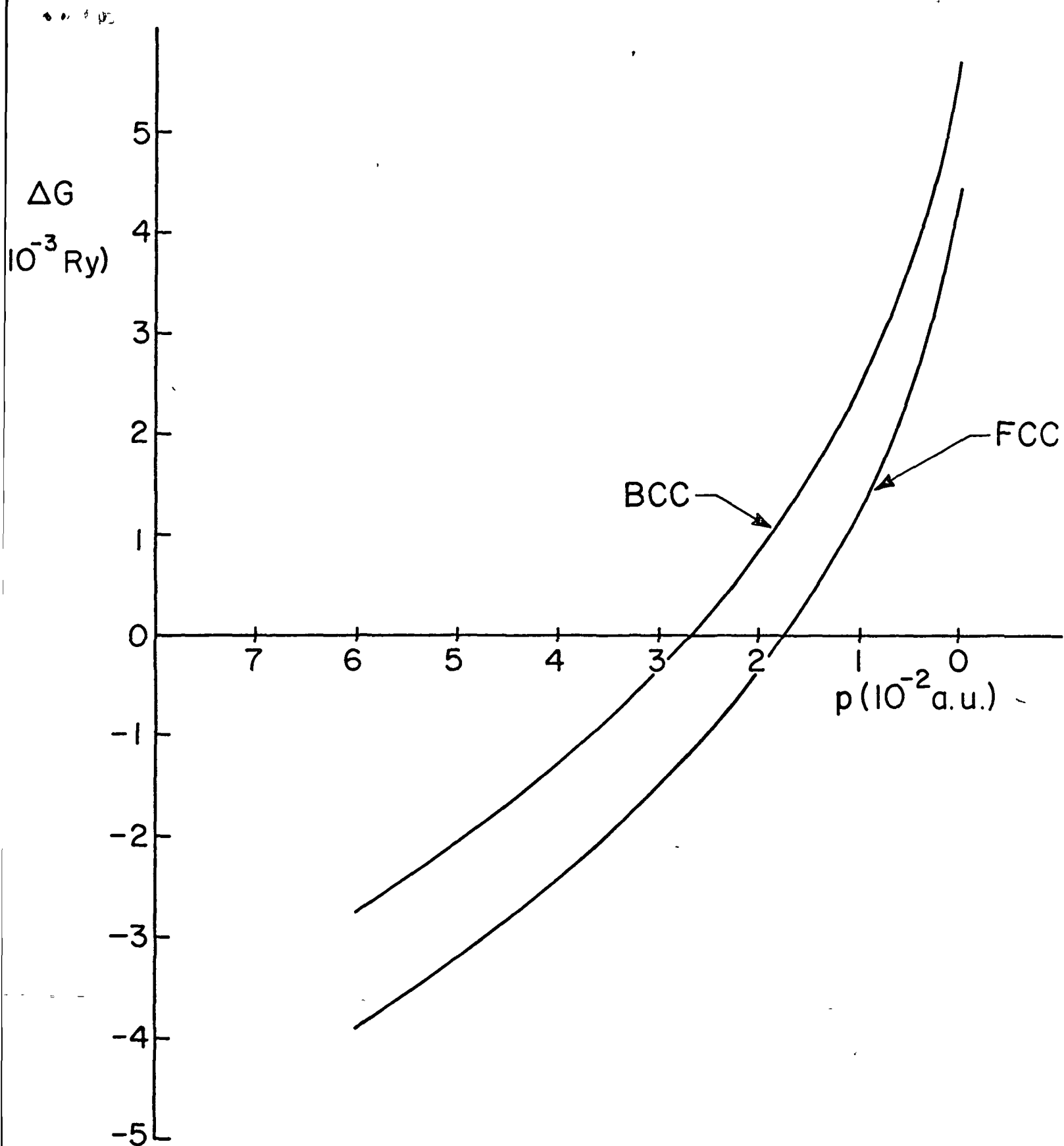


Fig. 9